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ON THE USE OF THE CONVENTIONAL CARBON FACTOR IN ESTIMATING SOIL ORGANIC MATTER

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Since the researches of Schulze, Wolff, Fresenius, and van Bemmelen, the use of the conventional carbon factor to estimate the organic matter in soils has been in general practice. The question has been raised at various times regarding the justification of this method for the determination of soil organic matter, and the object of this paper is to present more conclusive data on the problem. The following references include the more important studies in this field:

Schulze (6, p. 258) claims that 58 parts of carbon on an average represent 100 parts of organic matter in soil, and 60 parts represent 100 parts of humus.

Wolff (9) assumes that the percentage of carbon in "humus" is 58, and determines the organic matter of the soil by multiplying the organic carbon by the factor 1.724 or the carbon dioxide by 0.471.

Van Bemmelen (7) multiplies the amount of organic carbon by the factor 1.724 in order to obtain the organic matter in a soil.

Warington and Peake (8) give their results with three methods for the determination of organic carbon in soil. They find the relation of carbon to be fairly constant, the average being 79.9 per cent of carbon found by oxidation with chromic acid, 92.4 per cent by oxidation with potassium permanganate, for 100 yielded by combustion in oxygen. They also compare the organic matter of the soils studied, as determined by loss on ignition, to the organic matter calculated from the carbon found by combustion in oxygen, assuming with Schulze, Wolff and Fresenius that carbon is 58 per cent of the organic matter. In all cases the loss on ignition is considerably in excess of the organic matter calculated from the carbon factor, even when the soil has been dried at 150°C. For this reason these investigators consider it necessary to determine directly the percentage of carbon in order to measure with any degree of accuracy the organic matter present.

Loges (3) refers to the general use of the carbon factor among the German experiment stations in estimating soil organic matter. A large number of soils was studied and experimental data are tabulated showing the wide difference existing between the results obtained by oxidation with chromic acid and those secured by ignition. The results of Loges corroborate those of Warington and Peake. The lower values by the chromic acid method are attributed to the formation of some acetic acid.

Cameron and Breazeale (1) report their investigations on the organic matter in soils and subsoils as determined by their modified chromic acid method for estimating the organic carbon. In 1900 these investigators discovered in 32 out of 84 cases that the loss on ignition method gave a higher percentage of organic matter in the subsoils than in the corresponding surface soils. Finding combustion in a tube slow and unsatisfactory an improved chromic acid method was adopted. They conclude from their results that "there is not sufficient ground as yet for advocating the use of any other factor than the usually accepted one for the calculation of the organic matter from the carbon dioxide obtained in the combustion," and recommend the conventional factor as established by Wolff, Van Bemmelen, and Wollny.

More recently Gortner (2) states that "Inasmuch as the 'humus' extract of soils is undoubtedly a mixture of organic compounds, many of which are colorless and in all probability are extracted from unchanged plant or animal materials, and inasmuch as the soil pigment present in this solution probably rarely exceeds 40 per cent of the humus, a determination of the humus as ordinarily carried out appears to be wholly without scientific justification. The European method of reporting 'humus,' by making a determination of total organic carbon, appears to be far preferable."

In the fall of 1919 we undertook a thorough investigation of the percentage of carbon in soil organic matter, employing the modified rapid dry combustion method (5) devised especially for this investigation, which has been reported elsewhere. One-gram samples of soil were prepared for the determination in accordance with the method described by Rather (4). Inasmuch as the loss on ignition method for the determination of organic matter as modified by Rather appeared to offer certain advantages from the standpoint of accuracy, a further study of the carbon content of soil organic matter seemed justifiable. It was our belief that the method for the simultaneous determination of soil organic matter and organic carbon would enable us to make a very accurate study of the percentage of carbon in the total organic matter of soils, and the investigation of a considerable number of representative soils was undertaken.

The results secured are recorded in tables 1, 2 and 3.

It may be observed from table 1 that the average percentage of carbon in the organic matter is 49.26, approximately 9 per cent lower than the conventional factor. If the lower values for the West Virginia soils are excluded, the general average becomes 51.93. None of the soils investigated contained as high as 58 per cent of carbon in the organic matter, the percentage variations extending from 30.20 to 56.27. These results show that the use of the 58 per cent factor uniformly gives low values and may lead to very erroneous conclusions. It is questionable whether the use of any carbon factor deserves recommendation, but if such a factor is to be employed one based on 50 to 52 per cent of carbon would be more reliable.

Table 2 shows the percentage of carbon in the organic matter of the corresponding sub- and sub-surface soils of table 1. The average percentage of

TABLE 1

Nitrogen and carbon determinations in surface soils

REGISTER NUMBER	SOIL TYPE AND LOCATION	DEPTH OF SAMPLE	ORGANIC MATTER	CARBON IN ORGANIC MATTER	NITROGEN IN ORGANIC MATTER
		inches	*per cent*	*per cent*	*per cent*
2654	Lamoure silty clay loam (Iowa)	0–20	6.18	54.78	5.22
2656	Webster silty clay loam (Iowa)	0–15	3.62	50.62	5.60
2658	Wabash silt loam (Iowa)	0–20	6.18	55 44	5.85
2660	Carrington loam (Iowa)	0– 8	4.20	54 26	6.76
2662	Fargo silty clay loam (Iowa)	0–18	6.82	53.53	5.26
2669	Shelby loam (Mo.)	0–10	1.71	50.67	7.60
2672	Decatur silt loam (Mo.)	0–10	1.68	47.07	7.68
2675	Grundy silt loam (Mo.)	0–12	2.70	52.93	7.67
2678	Marshall silt loam (Mo.)	0–12	2.37	50.07	6.84
2682	Summit silt loam (Kan.)	0– 7	4.07	53.54	6.41
2684	Laurel very fine sandy loam (Kan.)	0– 7	2.73	54.41	6.05
2686	Marshall silt loam (Kan.)	0– 7	2.68	53.42	6.90
2688	Wabash silty clay loam (Kan.)	0– 7	4 22	53 54	5.16
2690	Oswego silt loam (Kan.)	0– 7	5.59	53.32	5.06
2712	Fargo clay loam (Minn.)	0– 8	6.12	55.90	6.55
2714	Gloucester loam (Minn.)	0– 8	1.72	50.56	6.57
2716	Carrington silt loam (Minn.)	0– 8	4.22	49.92	5.88
2718	Hempstead silt loam (Minn.)	0– 8	3.76	54 43	5 61
2720	Colby silt loam (Wis.)	0– 7	1.91	48 77	6 23
2722	Clyde sandy loam (Wis.)	0– 7	3.70	54 54	6.17
2724	Clyde loam (Wis.)	0– 7	5.26	54.64	6.86
2726	Clyde silt loam (Wis.)	0– 7	4.56	52.67	6.10
2728	Superior silt loam (Wis.)	0– 7	2.00	44.61	7.05
2730	Waukesha silt loam (Wis.)	0– 7	1.23	44 38	9.84
2732	Knox silt loam (Wis.)	0– 7	2.18	45.21	7.16
2734	Westmoreland silty clay (W. Va.)	0– 7	5.40	50.49	5.89
2738	Upshur clay (W. Va.)	0– 7	2.73	30.20	4.73
2740	Moshannon silt loam (W. Va.)	0– 7	2.44	33.01	6.27
2742	Huntington loam (W. Va.)	0– 7	5.34	36.89	5.28
2744	DeKalb silt loam (W. Va.)	0– 7	2.47	37.56	5.91
2746	Tyler silt loam (W. Va.)	0– 7	2.44	40.34	6.39
2748	Wheeling silt loam (W. Va.)	0– 6	3.50	34.51	5.46
2760	Barnes loam (N. Dak.)	0– 7	6.18	55.87	5.95
2764	Fargo clay (N. Dak.)	0– 7	8.05	53.51	4.98
2766	Bearden silt loam (N. Dak.)	0– 7	5.46	55.08	6.52
2791	Diablo clay (Cal.)	0–12	3.30	56.27	5.55
2792	Diablo clay adoba (Cal.)	0–24	1.38	49.02	6.01
Average				49.26	6.24

carbon is 39.16 for the lower soil depths, and 43.91 for the entire list as given in tables 1 and 2. The range of percentage variation in table 2 is from 13.33 (Upshur clay subsoil) to 56.55, the value for the Wabash silt loam subsoil.

TABLE 2

Organic matter in the sub- and sub-surface soils of those recorded in table 1

REGISTER NUMBER	SOIL TYPE AND LOCATION.	DEPTH OF SAMPLE	ORGANIC MATTER	CARBON IN ORGANIC MATTER
		inches	*per cent*	*per cent*
2655	Lamoure silty clay loam subsoil (Iowa)	20–36	1.14	46.64
2657	Webster silty clay loam subsoil (Iowa)	15–36	1.22	47.16
2659	Wabash silt loam subsoil (Iowa)	20–36	2.19	56.55
2661	Carrington loam subsoil (Iowa)	18–36	0.94	48.41
2663	Fargo silty clay loam subsoil (Iowa)	18–36	3.46	52.14
2667	Putman silt loam subsurface soil (Mo.)	10–18	0.86	27.73
2668	Putman silt loam subsoil (Mo.)	18–36	0.90	29.36
2670	Shelby loam sub-surface soil (Mo.)	10–16	0.66	35.61
2671	Shelby loam subsoil (Mo.)	16–36	0.51	33.62
2673	Decatur silt loam sub-surface soil (Mo.)	10–20	0.75	26.72
2674	Decatur silt loam subsoil (Mo.)	20–36	0.46	22.82
2676	Grundy silt loam sub-surface soil (Mo.)	12–18	1.03	42.09
2677	Grundy silt loam subsoil (Mo.)	18–36	0.81	28.08
2679	Marshall silt loam sub-surface soil (Mo.)	12–24	1.68	35.46
2680	Marshall silt loam subsoil (Mo.)	24–36	1.03	28.04
2683	Summit silt loam subsoil (Kan.)	7–20	2.46	38.56
2685	Laurel very fine sandy loam subsoil (Kan.)	7–20	1.07	49.82
2687	Marshall silt loam subsoil (Kan.)	7–20	1.56	27.04
2689	Wabash silty clay loam subsoil (Kan.)	7–20	3.32	53.33
2691	Oswego silt loam subsoil (Kan.)	7–20	1.94	50.45
2713	Fargo clay loam subsoil (Minn.)	8–36	0.53	49.94
2717	Carrington silt loam subsoil (Minn.)	8–36	0.51	30.47
2719	Hempstead silt loam subsoil (Minn.)	8–36	0.55	29.96
2721	Colby silt loam subsoil (Wis.)	7–36	0.35	31.55
2723	Clyde sandy loam subsoil (Wis.)	7–36	0.44	53.93
2725	Clyde loam subsoil (Wis.)	7–36	1.16	51.14
2727	Clyde silt loam subsoil (Wis.)	7–36	1.32	48.44
2729	Superior silt loam subsoil (Wis.)	7–36	0.60	27.27
2731	Waukesha silt loam subsoil (Wis.)	7–36	0.49	30.29
2733	Knox silt loam subsoil (Wis.)	7–36	0.75	34.17
2735	Westmoreland silty clay subsoil (W. Va.)	7–20	3.46	43.71
2739	Upshur clay subsoil (W. Va.)	7–20	1.37	13.33
2741	Moshannon silt loam subsoil (W. Va.)	7–20	1.11	25.92
2743	Huntington loam subsoil (W. Va.)	7–20	3.08	35.53
2745	DeKalb silt loam subsoil (W. Va.)	7–20	1.02	20.83
2747	Tyler silt loam subsoil (W. Va.)	7–20	1.04	27.92
2761	Barnes loam subsoil (N. Dak.)	7–18	3.13	52.44
2765	Fargo clay subsoil (N. Dak.)	7–18	4.22	48.97
2767	Bearden silt loam subsoil (N. Dak.)	7–18	2.64	51.03
2790	Dublin clay subsoil (Cal.)	12–36	2.40	51.42
2793	Diablo clay adoba subsoil (Cal.)	24–72	1.08	42.42
Average				39.16

Table 3 presents data on 13 soils selected at random from table 1. The second column gives the actual percentage of organic matter found in these soils. The third, fourth and fifth columns show the percentage of organic matter calculated on the basis of 58 per cent carbon, 49.26 per cent carbon, and 6.24 per cent nitrogen, the average value found for the percentage of nitrogen in the organic matter of the surface soils. It is obvious from an inspection of the deviation values shown in table 3 that those in the fifth column are the least significant. On this basis, therefore, the adoption of a conventional nitrogen factor would seem to be more satisfactory and would make it possible to estimate the organic matter in soils more readily than by the organic carbon determination.

TABLE 3

Organic matter found in soils compared with calculated determinations

REGISTER NUMBER	ORGANIC MATTER FOUND	ORGANIC MATTER BASIS OF 58 PER CENT CARBON WITH DEVIATION	ORGANIC MATTER BASIS OF 49.26 PER CENT CARBON WITH DEVIATION	ORGANIC MATTER BASIS OF 6.24 PER CENT NITROGEN WITH DEVIATION
2654	6.18	5.86 −0.33	6.89 +0.71	5.17 −1.01
2660	4.20	3.94 −0.26	4.64 +0.44	4.55 +0.35
2712	6.12	5.82 −0.30	6.86 +0.74	6.42 +0.30
2720	1.91	1.61 −0.30	1.90 −0.01	1.91 ±0.00
2722	3.70	3.49 −0.21	4.11 +0.41	3.66 −0.04
2726	4.56	4.15 −0.41	4.89 +0.33	4.46 −0.10
2728	2.00	1.54 −0.46	1.82 −0.18	2.26 +0.26
2730	1.23	0.95 −0.28	1.12 −0.11	1.94 +0.71
2738	2.73	1.42 −1.31	1.68 −1.05	2.07 −0.66
2742	5.34	3.43 −1.91	4.04 −1.30	4.52 −0.82
2746	2.44	1.70 −0.74	2.00 −0.44	2.50 +0.06
2791	3.30	3.21 −0.09	3.78 +0.48	2.94 −0.36
2792	1.38	1.17 −0.21	1.38 ±0.00	1.33 −0.05
Average....	3.47	2.94	3.47	3.36

SUMMARY

An investigation of the carbon content of the organic matter of 37 surface soils secured from seven different experiment stations has been made by a modified rapid dry combustion method devised for the simultaneous determination of soil organic matter and organic carbon. Similar data also have been secured for the corresponding sub- and sub-surface soils.

The data presented show that the use of the generally accepted conventional factor uniformly gives low results.

The percentage of organic carbon in the surface soils varied from 30.20 to 56.27, the general average being 49.26, which is about 9 points below the accepted value.

It is very doubtful whether the use of any arbitrary carbon factor is justifiable. If one is to be employed more accurate results will be obtained if it is based on 50 to 52 per cent of carbon.

The data presented on the percentage of nitrogen indicate that the adoption of a conventional nitrogen factor would give more reliable information regarding the organic matter content of a soil, and certainly the nitrogen determination is more common and less difficult.

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THE RELATION OF HYDROGEN-ION CONCENTRATION IN SOILS TO THEIR "LIME REQUIREMENT"

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INTRODUCTION

Every state in the humid section of the United States is concerned with the acidity of soils. The nature of the phenomenon has not been understood and considerable controversy exists as to what constitutes this acidity. It has been attributed to the presence of acids, mineral and organic, to colloidal material, to adsorption and absorption, and to the presence of specific compounds. More recently the presence of hydrogen ions has been demonstrated. This is a property accompanying all acid reactions, hence their presence shows that soil acidity is actual acidity and is not a property due to the complicated theoretical phenomena previously advanced.

The presence of hydrogen ions has been demonstrated and their concentration has been measured by several investigators. Gillespie (5), using a hydrogen electrode, showed that of twenty-two samples tested, seventeen were acid and five alkaline, the pH values varying from 4.55 to 8.7. Sharp and Hoagland (18), using somewhat similar apparatus, studied twenty-four soils and found nine acid and fifteen alkaline with a variation in hydrogen-ion concentration of pH 3.7 to pH 9.7. Plummer (15) found a range of pH 4.04 to pH 9.68 in sixty-eight soils tested by the hydrogen electrode. Morse (14), in determining the hydrogen-ion concentration of different fertilizer plots by a colorimetric method, found that different fertilizers affected the acidity, sulfate of ammonia giving a pH value of 4.9 as compared with 5.2 for the check plot and 6.4 for a limed plot. Knight (12), using a hydrogen electrode, demonstrated the presence of hydrogen ions but in measuring his concentrations he used salt solutions, for some reason, so his measurements are not comparable with those of others.

Hydrogen ions may come from any of the organic or inorganic acids, from acid salts or from salts of weak bases and strong acids. Acid soils may contain all of these. The bases of the originally alkaline soils were converted into soluble salts by weathering and used by plants or leached out, leaving the less soluble acid silicates and silicates of iron and aluminum. Under these conditions nitric, sulfuric and many organic acids may accumulate from bacterial action. It is probable that the main sources of hydrogen ions are the acid silicates and the salts of the weak bases, iron and aluminum.

The diversity of opinions as to the nature of soil acidity has led to the formulation and adoption of numerous methods for its measurement. These different methods give such widely varying results that the correctness of any one of them is seriously in doubt. One investigator looks for "apparent acidity," another for "adsorption acidity," another for "real acidity," while all term their results "lime requirement."

Among the most widely adopted methods for the measurement of lime requirement are those of Hopkins (9), Veitch (24), and Tacke (20). These have all been modified by different workers so that there are now numerous methods based upon their principles. Two other methods should be noted also, one by Truog (21) because of its simplicity and practical applicability and another by Bouyoucos (2) because it measures not only the lime needed to neutralize the acidity but also the amount beyond this point which the soil will take up.

There are two general methods for the determination of hydrogen-ion concentrations in soils, one by the use of indicators and the other more accurate, by means of the hydrogen electrode. Gillespie (6), Wherry (25), and Van Altstine (23) have suggested colorimetric methods, including lists of indicators with their pH values, standard solutions and color comparators, especially applicable to soil studies. Such methods, while not so accurate as the hydrogen-electrode methods, are more rapid and probably of sufficient accuracy for many investigations. Almost as many forms of hydrogen electrodes have been devised as there are people working with them. They are compared with a great variety of standard electrodes, including many calomel and standard hydrogen cells and the electromotive force of such chains may be measured by several potentiometer methods and by more simple arrangements such as the one proposed by Hildebrand (7).

The comparative value of the two determinations, the lime requirement and the hydrogen-ion concentration, has not been fully determined. The lime-requirement methods have been in use for some time and a great amount of data is available to show that in general, when soils are found to need lime they are benefited by such applications, especially for certain crops, the legumes. This fact is so generally conceded that it is not necessary to discuss the matter. However, there are numerous cases where clover has been known to grow well on soils showing fairly high lime requirements and others where small applications of lime were as beneficial as larger ones.

Then, too, the wide variations in results by the different methods bring up the question as to what is the correct amount to apply in a definite case. The hydrogen-ion determination does not indicate the lime requirement directly but shows only the strength or intensity of the acidity. The methods for such determinations have been so recently put into use that no data are available as to its practical applications. A large amount of data has accumulated, however, to show that, in culture media, the strength of the acid and not the quantity present is the factor affecting bacterial and mold growth. Enzyme

activity also has been shown to be dependent on hydrogen-ion concentration. So positively is this proven that the adjustment of the reaction of such media is now made on this basis and not on the basis of titratable acid. Clark and Lubs (4) in 1917 collected and summarized sufficient data on this subject to prove the necessity of such adjustments. Many other workers have since shown conclusively their importance. If this is true of the lower organisms it is highly probable that the higher plants also are subject to the same factors. Wherry (25) makes the statement that, "Only the hydrogen ions developed directly by water in the soil can have any influence on the growth of plants." Hoagland (8) has studied the effect of hydrogen ions on the growth of barley seedlings and Joffe (10) their effect on alfalfa. Each found a range of hydrogen-ion concentrations which was favorable to the growth of the plants and concentrations on either side that were injurious.

From all of the foregoing considerations the question arises, "What is the relation between lime requirement as determined by the various methods and hydrogen-ion concentration?" If there is a definite relationship, as Blair and Prince (1) have shown to exist in the plots at the New Jersey station, we can interpret the data secured by lime requirement methods in terms of hydrogen-ion concentration. If there is no such relation, as might be indicated in the work by Joffe (11), then the inconsistencies of the data from lime requirement results may be explained.

In an attempt to answer this question lime requirement and hydrogen-ion conentration determinations have been made on fifty widely different soils. The results secured follow:

EXPERIMENTAL PROCEDURE

Fifty soils were selected from samples collected in connection with the soil surveys of seven different counties. Twenty-two different series inluding four different textures are represented, giving a wide variety of types for study. The types are listed in table 2.

The lime requirement of each sample was determined by both the Veitch and Truog methods. Hydrogen-ion concentrations were measured by the use of a hydrogen electrode.

The Veitch method was used because it has probably been more widely adopted and has been used as a standard for comparison of other methods more universally than any other of the lime requirement tests. It has been a standard method in this laboratory for several years.

The logical use of lime water in only sufficient amounts to bring about an alkaline reaction and the fact that results somewhat comparable with actual field tests are possible, have been just causes for its popularity. However, it has three serious disadvantages that have drawn to it very severe criticism. First, it is a long and tedious test applicable only in a laboratory; second, it shows only the amount of lime needed to give a reaction alkaline to phenol-

phthalein, an indicator which changes at a point quite toward the alkaline side of neutral; third, and very much the most serious disadvantage, it is so sensitive to very slight variations in its manipulation that it is almost impossible to obtain concordant results except by long and tedious trials so that the results obtained by two different workers can not be accurately compared. This last criticism has been demonstrated by Stephenson (19) and Robinson (16).

Considerable difficulty was encountered in this work in securing results which could be depended upon as correct. An attempt was made to determine the lime requirements to within 200 pounds, but this, except in cases of small requirements, was abandoned and a variation of 400 pounds was allowed with most samples and even 800 pounds with soils showing need for

TABLE 1

Illustrating the difficulty in securing duplicate tests with the Veitch method

SOIL NUMBER	LIME WATER*	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION	LIME WATER	REACTION
	cc.		*cc.*		*cc.*		*cc.*		*cc.*		*cc.*		*cc*		*cc.*		*cc.*	
	10	Acid	8	Acid	8	Acid	9	Acid	10	Acid	10	Acid	11	Alk.	10	Acid		
15	15	Alk.	12	Alk.	10	Acid	10	Acid	11	Acid	11	Acid	12	Alk.	11	Alk.		
	20	Alk.	16	Alk.	12	Alk.	11	Acid	12	Alk.	12	Acid	13	Alk.	12	Alk.		
	10	Acid	20	Acid	16	Acid	18	Acid	18	Acid	18	Acid	18	Acid	19	Alk.	19	Acid
23	15	Acid	25	Alk.	20	Alk.	20	Acid	19	Alk.	19	Acid	19	Acid	20	Alk.	20	Alk.
	20	Acid	30	Alk.	24	Alk.	22	Acid	20	Alk.	20	Alk.	20	Acid	21	Alk.	21	Alk.
	25	Alk.	15	Acid	18	Acid	22	Acid	24	Acid	24	Alk.	23	Acid	23	Acid		
30	30	Alk.	20	Acid	22	Acid	24	Acid	26	Acid	26	Alk.	24	Acid	24	Acid		
	35	Alk.	25	Alk.	26	Alk.	26	Acid	28	Acid	28	Alk.	25	Alk.	25	Alk.		

*Each cubic centimeter of lime water is equivalent to 200 pounds of limestone, $CaCO_3$ per acre of 2,000,000 pounds of soil.

the largest amounts of lime. Apparently good results could be secured easily but attempts to duplicate the test frequently failed. Results in table 1 illustrate the difficulties encountered in checking tests with three representative samples.

In all the work double-distilled water was used and extreme care was taken to see that all manipulations were as nearly the same as possible at all times.

The results reported in table 2 and used throughout this article were accepted only after repeated trials, as shown in the above table, had proved their accuracy.

The Truog test was compared with the hydrogen-ion determinations because it has largely supplanted the Veitch method at this station for routine analyses and tests for field applications. It is also widely used for practical tests out-

side of the experiment stations. The lime requirements reported in table 2 are results of two agreeing tests.

The hydrogen-ion determinations were made with a hydrogen electrode, patterned after the one used by Sharp and Hoagland (18), modified slightly as shown in figure 1, A. The platinum electrode consists of a $\frac{3}{8}$-inch square of heavy platinum foil coated with platinum black deposited from a 3 per cent solution of platinic chloride containing a trace of lead acetate. Two hydrogen electrodes were held in a shaking device, as illustrated in figure 1 B, which was operated by an electric motor regulated so as to give between 160 and 180 complete strokes, $\frac{3}{4}$-inch long, a minute. Hydrogen was generated electrolytically and purified by passing over heated, platinized asbestos. Connection was made to a normal calomel electrode through a saturated potassium chloride solution by means of a tube filled with agar made up with a saturated potassium chloride solution.

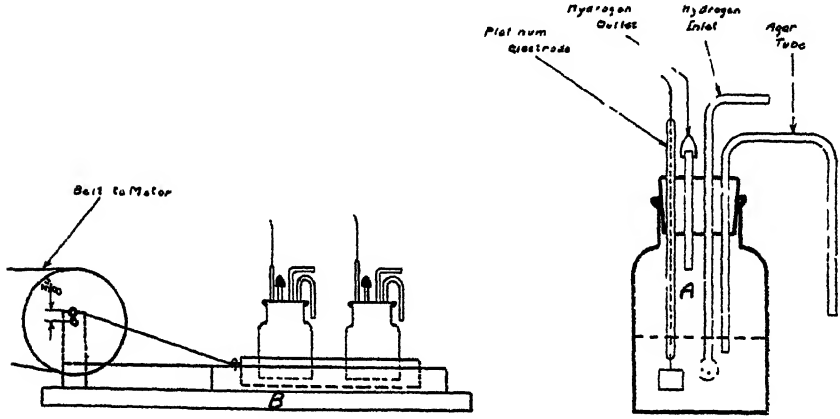

FIG. 1. HYDROGEN ELECTRODE AND SHAKER

The electromotive force of the chain was measured by an apparatus as suggested by Hildebrand (7), using an accurate voltmeter calibrated from 0 to 1.5 volts by intervals of .01 volt and readable to 2 millivolts. Ten grams of soil with 25 cc. of neutral water were used for the determinations. Readings on duplicate samples checked to within 5 millivolts in every case and frequently checked exactly. The accuracy of the determinations is within .05 of a pH value.

The hydrogen-ion concentrations of the fifty samples are reported in table 2 in pH values, a term which has been used so much of late that there is no necessity for its explanation here. However, Schmidt and Hoagland (17), Clark and Lubs (4) and Leeds and Northrup (13) explain in detail the method by which it is obtained. It should be remembered that 7.0 pH is neutral and that a lower pH value shows acidity, corresponding to a higher hydrogen-ion concentration, while a greater value means alkalinity with a correspondingly lower hydrogen-ion concentration.

TABLE 2

Results of Veitch, Truog and hydrogen-ion determinations and analyses of soils on basis of acre of 2,000,000 pounds

NUMBER	SOIL TYPE	VEITCH LIME REQUIREMENT	TRUOG LIME REQUIREMENT	(H^+) IN P_H	ORGANIC CARBON	NITROGEN	CARBON – NITROGEN RATIO, N=1	PHOSPHORUS
		lbs.			*lbs.*	*lbs.*		*lbs.*
1	Sarpy loam	0	negative	7.78	22,700	1,980	11.4	2,195
2	Thurston sandy loam	0	negative	7.73	20,500	1,180	17.4	1,185
3	Sarpy silt loam	0	negative	7.68	29,983	2,590	11.6	1,481
4	Wabash silt loam	0	negative	7.56	53,631	4,180	12.8	1,669
5	Carrington sandy loam	0	negative	7.54	30,977	2,630	11.8	1,024
6	Cass fine sandy loam	0	negative	7.30	27,237	1,770	15.4	808
7	Jackson silt loam	0	negative	7.20	29,721	2,370	12.4	660
8	Clyde silty clay loam	0	negative	7.05	17,581	890	19.8	593
9	Wabash loam	0	very slight	6.86	46,137	3,800	12.2	822
10	Carrington loam	600	very slight	6.41	60,060	4,800	12.5	1,091
11	Lindley fine sandy loam	800	very slight	5.83	13,377	1,120	12.0	485
12	Hancock loam	1,600	slight	6.88	75,238	5,650	13.6	902
13	Carrington loam	2,000	strong	5.70	27,627	2.380	11.6	902
14	Knox fine sandy loam	2,000	slight	4.85	10,592	720	14.7	942
15	Lindley sandy loam	2,200	medium	5.33	12,175	890	13.7	687
16	Lindley loam	2,400	slight	5.51	23,478	1,740	13.5	745
17	Plainfield loam	2,800	slight	5.39	21,294	1,310	16.3	808
18	Cass sandy loam	3,000	medium	5.34	19,929	1,120	17.8	1,010
19	Buckner fine sandy loam	3,000	strong	5.02	37,128	3,090	12.0	889
20	Wabash silt loam	3,200	negative	7.30	38,493	2,980	12.9	1,736
21	Plainfield sandy loam	3,200	medium	5.36	23,641	1,340	17.6	808
22	Wabash fine sandy loam	4,000	slight	6.36	73,381	5,500	13.4	1,913
23	Carrington fine sandy loam	4,000	medium	5.38	37,401	2,740	13.7	943
24	Shelby loam	4,200	very strong	5.41	27,027	2,210	12.2	795
25	Shelby loam	4,400	strong	5.53	36,145	2,960	12.2	889

26	Carrington sandy loam	4,400	very strong	5.02	28,665	1,960	14.6	741
27	Carrington silt loam	4,800	medium	6.04	43,680	3,670	11.9	1,387
28	Buckner loam	4,800	very strong	5.53	52,962	3,950	13.4	1,131
29	O'Neill loam	4,800	strong	5.04	33,688	3,700	9.1	1,428
30	O'Neill sandy loam	5,000	very strong	5.00	25,880	1,460	17.7	876
31	Lindley silt loam	5,200	slight	5.90	27,846	2,070	13.4	660
32	Clinton silt loam	5,200	medium	5.33	19,110	1,760	10.8	700
33	Waukesha silt loam	6,800	medium	6.00	46,137	3,480	13.2	1,495
34	Judson silt loam	7,600	medium	5.73	49,140	3,600	13.7	1,414
35	Carrington loam	7,600	strong	5.36	48,590	4,180	11.6	1,050
36	Marshall silt loam	8,400	medium	5 58	53,344	4,360	12.2	929
37	Tama silt loam	8,800	slight	5.36	36,036	2,520	14 3	902
38	Bremer silt loam	9,600	medium	6 20	107,452	8,380	12.8	2,074
39	Clinton silt loam	9,600	slight	5 53	34,343	2,680	12 8	1,100
40	Clinton silt loam	9,600	medium	5.36	33,961	2,730	12 5	996
41	Carrington loam	10,800	very strong	5.11	50,641	4,410	11 5	1,024
42	Grundy silt loam	11,200	medium	5.66	96,587	4,860	20 0	1,118
43	Grundy silt loam	12,000	strong	5.11	56,511	4,160	13.6	1,387
44	Carrington loam	12,800	very strong	5.14	62,244	5,190	12.0	1,145
45	Tama silt loam	12,800	strong	4.94	54,873	4,480	12.3	1,414
46	Putnam silt loam	12,800	very strong	4 84	34,944	2,820	12.4	969
47	Tama silt loam	13,600	medium	5.19	59,623	4,600	13.0	1,306
48	Wabash silt loam	14,400	strong	5.22	42,970	3,530	12.2	983
49	Wabash loam	18,000	strong	5.56	113,677	9,590	11 9	1,913
50	Bremer loam	24,000	very strong	4.55	76,767	6,200	12.4	1,684

EXPERIMENTAL RESULTS

In table 2 and graphically in figure 2 is shown the relation of the hydrogen-ion concentrations to the Veitch lime requirement of each of the fifty samples. The samples have been arranged in the table and for making up the graph in the order of increasing Veitch lime requirement. Where samples show the same lime requirement the one having the highest pH value is given first.

It will immediately be noted that there is no apparent relationship between the results of the two determinations except that all of the samples having no lime requirement, except no. 9, show an alkaline reaction as measured by the hydrogen electrode and all of the samples with lime requirements, except no. 20, show acid with the electrode. It was found that the soils with a low

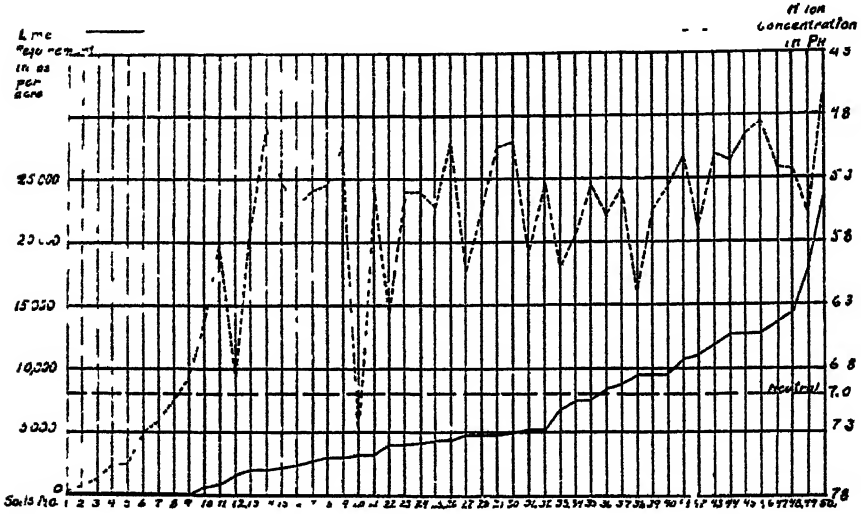

FIG. 2. RELATION OF VEITCH LIME REQUIREMENT TO HYDROGEN-ION CONCENTRATION

lime requirement had as high a hydrogen-ion concentration as those in need of the larger amounts of lime, in fact no. 14, with a lime requirement of only 2000 pounds has the highest hydrogen-ion concentration of all the samples except no. 50. Even the general trend of the line representing hydrogen-ion concentrations bears no relation to the line representing lime requirement. It is evident that in considering soils of different types there is no relation between acidity, as measured by the hydrogenelectrode, and so-called "acidity," as measured by the Veitch method.

In table 2 and figure 3, the results of Truog tests as related to hydrogen-ion concentrations are shown. In figure 3 as in figure 2, the samples are arranged in order of increasing lime requirement. This was done by laying the test papers in a row and arranging them according to the intensity of color. The arrangement was checked by three other observers. The points on the

curve indicating very slight, medium, strong and very strong acidity were determined by selecting the test papers corresponding to the colors on the Truog chart (21). Lines connecting these points, representing the acidity of intervening samples, give a fairly regular curve for the Truog tests.

From figure 3 it is evident that here again there is no definite relationship between the results obtained by the Truog test and the hydrogen electrode. It will be noted, however, that there is somewhat better correlation than in figure 2. All the samples with no lime requirement show alkaline by the electrode method and all those in need of lime show acid. Also it is very evident that the general trend of the hydrogen-ion line is more nearly parallel to the Truog test line than it was to the Veitch test line. Apparently the Truog method has more of a tendency to indicate the strength of the acids than has the Veitch test.

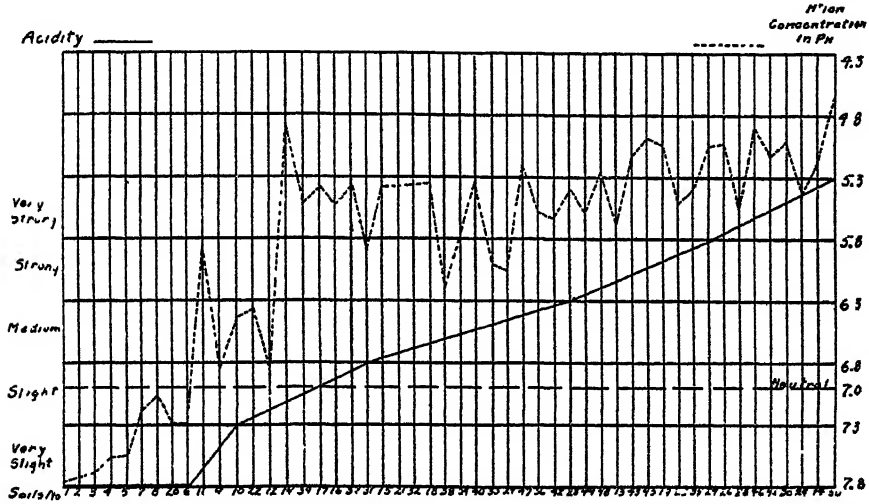

FIG. 3. RELATION OF TRUOG ACIDITY TO HYDROGEN-ION CONCENTRATION

Considering both tests, however, the conclusion is necessarily reached that lime requirement is not very closely related to the strength of the soil acids when soils of various types are compared. When this lack of relationship became evident an explanation for it was sought.

The soils were separated into four classes, silt loams, loams, fine sandy loams and sandy loams according to texture. One silty clay loam, no. 8, was included with the silt loams. The samples in each class were arranged according to increasing lime requirements by both methods and plotted in figures 4 and 5. It is readily seen from these diagrams that texture has a great influence on the relation between the lime requirement and hydrogen-ion concentration. With the finer textured soils the trend of the lines representing the two determinations is nearly parallel and the lines are not far apart. This is especially true of the Truog tests. It will be noted, too, that the finer

soils include the ones with the higher lime requirement. In the case of the coarser textured samples the lines are very far apart. These have rather low lime requirement but very high hydrogen-ion concentration. Even though

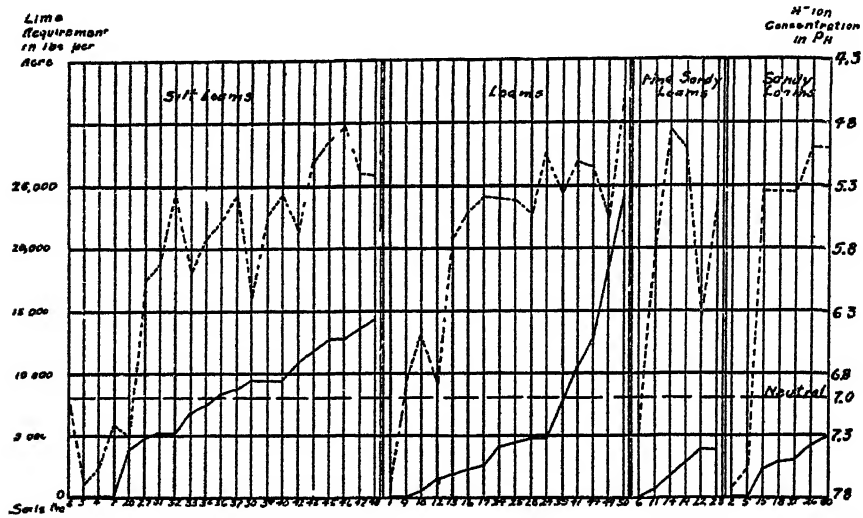

FIG. 4. RELATION OF VEITCH LIME REQUIREMENT TO HYDROGEN-ION CONCENTRATION AS AFFECTED BY SOIL TEXTURE

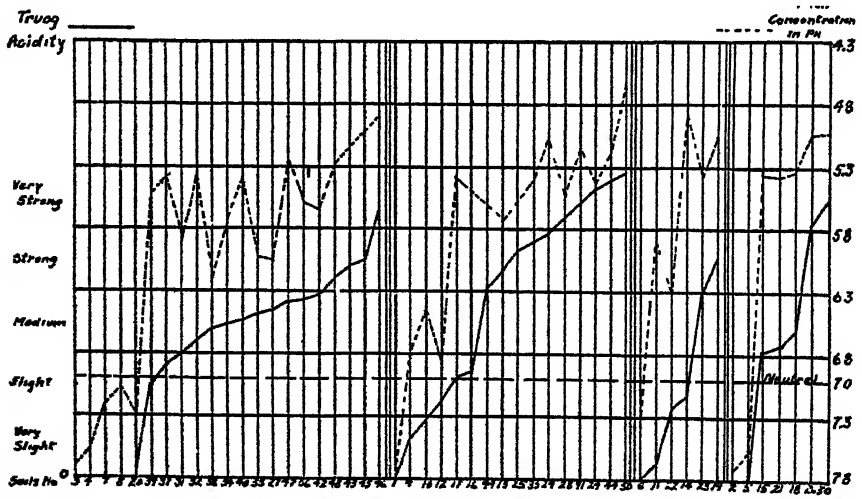

FIG. 5. RELATION OF TRUOG ACIDITY TO HYDROGEN-ION CONCENTRATION AS AFFECTED BY SOIL TEXTURE

texture explains some of the irregularities in the relationship between the two determinations, there is evidently some other factor which has even greater influence, since the line representing hydrogen-ion concentration is still very uneven. This is quite pronounced in the case of both tests.

When a line representing the organic carbon content[1] of each soil is drawn in, as in figure 6, the influence of organic matter on the intensity of the acidity is very evident. When the organic matter content is very low, the hydrogen-ion concentration is very high and when the organic content runs very high the hydrogen-ion concentration as compared to the lime requirement is very low. These relationships are very strikingly true in samples 12, 14, 15, 18, 22, 32, 38, 42, 46 and 49.

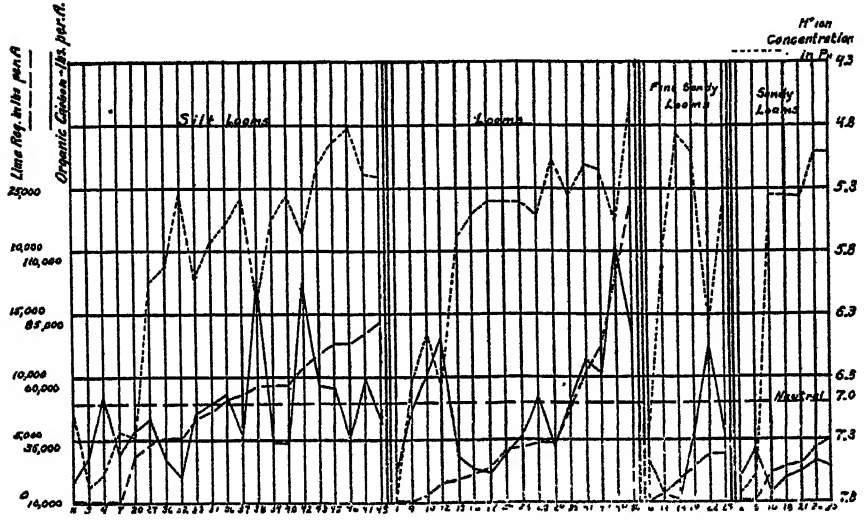

FIG. 6. RELATION OF VEITCH LIME REQUIREMENT AND HYDROGEN-ION CONCENTRATION IN SOILS OF SIMILIAR TEXTURE TO ORGANIC CARBON CONTENT

DISCUSSION OF RESULTS

From the brief outline of results given, it is evident that the Veitch method does not in any way indicate the intensity of the acidity. It may measure the amount of lime which will be taken up by a soil but this seems to have little relation to the strength of the soil acids. The Truog test in a slight measure does indicate the strength of the acids. In figure 7 the Veitch, Truog and hydrogen-ion determinations are plotted together. From this graph it seems that the results of the Truog test are a combination of the other two determinations. With low lime requirement and high hydrogen-ion concentration, the Truog test shows a higher lime requirement than the Veitch, and the opposite is true. Truog (22) has demonstrated this by the use of his acidity method and claims a superiority for practical use for his test in that it gives what he terms "crop-injurious acidity."

[1] The analyses of these soils were made by Mr. J. T. Auten for the Soil Survey reports; the author wishes to express his appreciation to Mr. Auten for the use of his results.

That soil acids do not accumulate in the coarser textured soils to so great an extent as in the heavier soils but that those that are present are stronger, is clearly shown. Both the amount and strength of the acids present can be explained by the content of clay and silt particles in the individual soils. These particles are made up of the more finely divided silicates, hence are more readily weathered to form large quantities of acid silicates which can react with lime water to show apparent acidity. The coarser material of the lighter soils is not so subject to weathering, as was shown by Brown and Johnson (3) who found that grinding the coarser soils reduced the lime requirement; thus acid silicates do not accumulate to so great an extent in these lighter soils. Then too, much of the coarse material consists of silica, SiO_2,

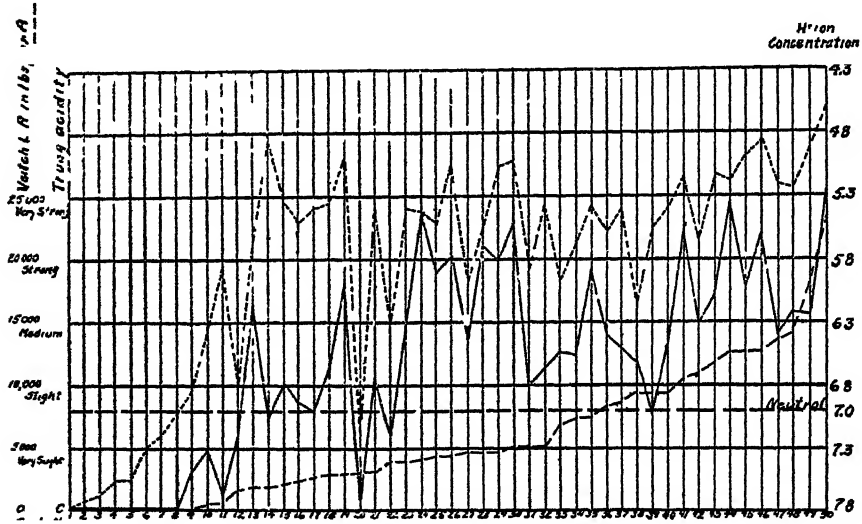

FIG. 7. RELATION OF VEITCH, TRUOG AND HYDROGEN-ION DETERMINATIONS

which is too inert to react with lime water. Hence the greater source of potential acidity is found in the heavier soils.

On the other hand, the quantity of fine material present affects the strength of the acids in two ways. First, it is a recognized fact that coarser, more open soils are more easily and rapidly weathered and leached than the heavier soils. Thus the bases in the finer particles in the sandy soils will be more nearly completely removed than in the finer textured soils. This would affect the strength of the soil acidity in that the degree of removal of base would determine the amount of hydrogen-ions liberated. This may be illustrated by the titration curve for phosphoric acid where each of the acid salts, KH_2PO_4 and K_2HPO_4, gives rise to a definite hydrogen-ion concentration as is shown by Clark and Lubs (4). Thus the different acid salts formed in the weathering of the silicates would give rise to different hydrogen-ion concentrations; the less the amount of base present in each molecule the more intense would be

the acidity. Hence, with sandy soils which would be more highly weathered, we would expect a higher hydrogen-ion concentration.

The second effect might be due to "buffer" action of the clay. Several acid salts show this property, an ability to resist changes in hydrogen-ion concentration on the addition of acids or alkalis. This, too, is illustrated by the action of the phosphate salts in the experiment referred to above. When either of the acid phosphates are present, additions of potassium hydroxide have little effect on the pH value of the solution until all the salt present is changed over to another form. In soils the acid silicates may act as "buffers." This effect would be proportional to the amount of silicates present and their degree of weathering, which in turn would depend on the texture of the soil. In a soil containing more clay, consequently more silicates in a less weathered condition, the buffer effect would be greater. Hence, the accumulation of nitric, sulfuric and organic acids, and even the greater weathering and consequent hydrogen-ion liberation of some of the soil particles, would affect the hydrogen-ion concentration of the heavier soils less than the sandier ones.

The influence of the organic matter also may be explained by its "buffer" action. Organic materials are known to possess a very considerable "buffer" action, as has been shown by Clark and Lubs (4). Thus, with soils containing the larger amounts of organic carbon, we would expect to find the hydrogen-ion concentration very markedly depressed, while with smaller quantities no such effect would be obtained.

The older statements, that soil acidity was due entirely to organic acids, seem to be quite definitely discredited by these results, since the larger amounts of organic matter depress rather than increase the acidity. These statements are further contradicted when the carbon-nitrogen ratio, a widely adopted measure of the decomposition of organic matter, is plotted against the acidity, as in figure 8. It is very evident that the carbon-nitrogen ratio bears no relation to the acidity, hence, the oxidation of the organic matter with the supposedly consequent accumulation of organic acids can not be a cause of soil acidity in these soils. It must be noted, however, that these are mineral soils and the same would not hold true for peats and mucks.

Since the acidity could not be explained by the presence of organic acids, it was sought to prove it was due to weathering and subsequent removal of bases. The only index to such action available at present was the phosphorus content. This is only a rough index and its value was recognized as questionable. However, in these soils, all formed from similar materials, although laid down by different agencies at different times, the amount of phosphorus present should be, in general, proportionate to their loss of bases. Plotting this against the acidity and knowing it could in no way be a cause for acidity but only an approximate index to the cause in soils of similar texture, the results as shown in figure 9 were obtained. Here it is seen that where the phosphorus content is high, showing supposedly less weathering and loss of bases, the intensity of acidity is much less. This not only indicates that soil

acidity is due to weathering with subsequent loss of bases and the consequent formation of acid silicates, but substantiates the reasons given previously as to why the coarser soils are more intensely acid than the finer ones.

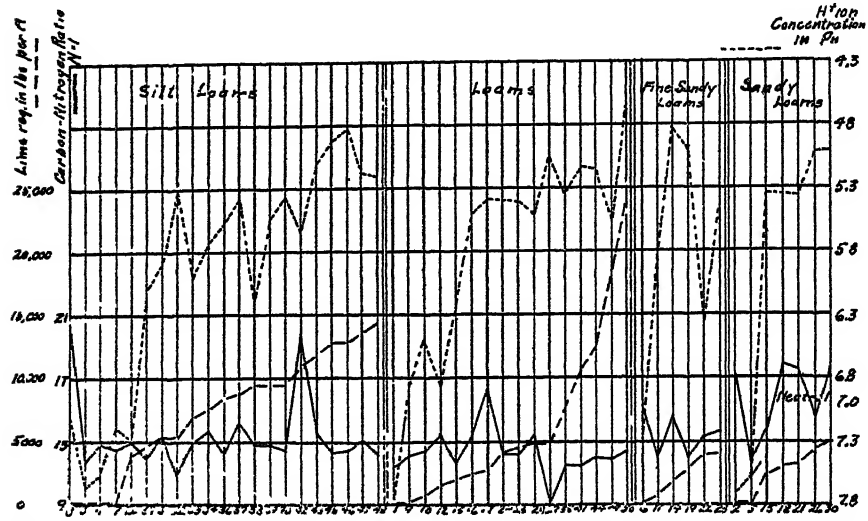

FIG. 8. RELATION OF VEITCH LIME REQUIREMENT AND HYDROGEN-ION CONCENTRATION IN SOILS OF SIMILIAR TEXTURE TO CARBON-NITROGEN RATIO

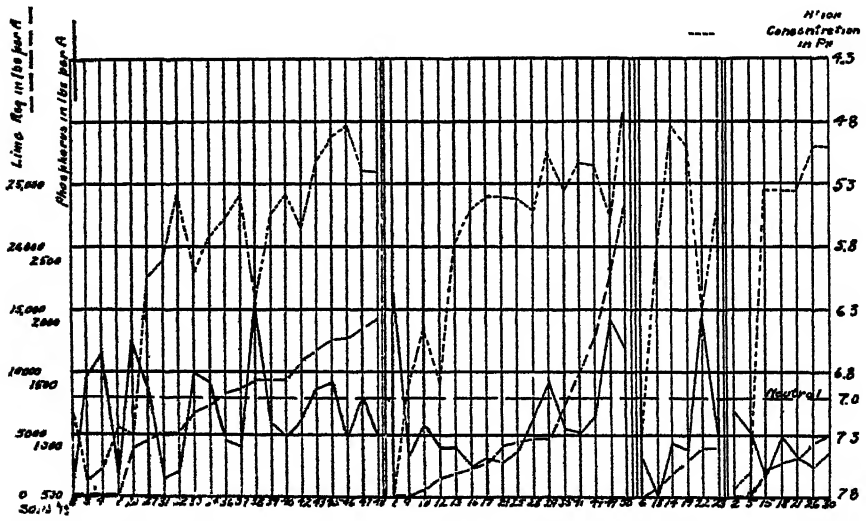

FIG. 9. RELATION OF VEITCH LIME REQUIREMENT AND HYDROGEN—ION CONCENTRATION IN SOILS OF SIMILAR TEXTURE TO PHOSPHORUS CONTENT

From all these considerations, it is plainly evident that, in soils as a whole, the apparent quantity of acid or the lime requirement has no relationship to the intensity or strength of acids present or the hydrogen-ion concentration.

This substantiates the inferred conclusions of Joffe (11) that sands and clays vary in relation between these two factors. However, for soils of the same type, that is, the same texture, age, formation, and color or organic-matter content, the two factors may bear a close relationship to each other. This explains the conclusions of Blair and Prince (1) who found that there was a definite relation between the lime requirement and hydrogen-ion concentration, working on the series of plots at the New Jersey station.

SUMMARY

Working with fifty samples of widely varying types it was found that:

1. As a whole there was no relation between the lime requirement as determined by the Veitch method and the hydrogen-ion concentration as measured by the hydrogen electrode.
2. The Truog method of measuring the lime requirement gave results which were a combination of the Veitch lime requirement and the hydrogen-ion concentration.
3. In soils of similar type there is a relation between the apparent quantity of acids and the strength of the acids.
4. Soil acidity in mineral soils is apparently due to weathering and leaching rather than the accumulation of organic acids.
5. Clay particles and organic matter act as "buffers" to keep the hydrogen-ion concentration down.

The buffer effect of these two materials is being further studied, as is also the proof of the statement that soil acidity is due to the weathering and leaching and consequent formation of acid silicates.

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ALUMINUM SALTS AND ACIDS AT VARYING HYDROGEN-ION CONCENTRATIONS, IN RELATION TO PLANT GROWTH IN WATER CULTURES

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INTRODUCTION

While there is a rather extensive literature upon the subject of the injurious effect of various acids and of aluminum salts upon plants in water cultures, there are so many variables which may affect plant growth that it is difficult to correlate the results obtained by different investigators. One of the factors which may cause a great variation in growth is the kind of nutrient solution and the method of using it. Without doubt this factor is one of the most important. There are very many combinations of various salts, proportions, and strengths which have been used, as well as sizes of containers and periods of frequency of changing the nutrient—all of which may vary the results obtained. The purity of the distilled water as well as that of the salts varies greatly. The kind of plant grown, the uniformity of the seed, and its freedom from, or affection by, disease may often cause variation in results.

Abbott, Conner and Smally (1) found in 1913 that solutions of aluminum nitrate and nitric acid were toxic to corn seedlings in dilute nutrient solutions. The toxicity of the aluminum nitrate was found to be approximately equal to that of nitric acid of the same normality. They suggested that the acid radical might be the toxic agent. Miyake (6) in 1916, in a study of the effect of aluminum chloride and hydrochloric acid on the rice plant in distilled water, found that the toxicity of aluminum chloride was equal to that of hydrochloric acid of the same normality. He determined the hydrogen-ion concentration of the solutions and found that the aluminum salt was more toxic than the acid at the same hydrogen-ion concentration and concluded that aluminum itself in some way was toxic. Hartwell and Pember (3) in 1918, after considerable work to find a suitable nutrient, found that, while aluminum sulfate was of equal toxicity toward rye as was sulfuric acid, barley was much more affected by aluminum salts than by an acid of the same hydrogen-ion concentration. They concluded that the toxicity of aluminum salts on barley is attributable largely to the aluminum.

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EXPERIMENTAL

With the object in view of investigating the relative toxicity of hydrogen ions and aluminum ions in a series of water cultures with aluminum salts and their corresponding acids, under controlled conditions, with seedlings of several cereals, experiments were started in 1919. In a first series of tests the grain was germinated in white moist silica sand, then washed and transferred to wide-mouth bottles of 480 cc. capacity. Paraffined cork stoppers were grooved on the sides and three seedlings held in place by rubber bands. In some preliminary tests the barley seedlings were partially affected by *helminthosporium* and *fusarium* enough to confuse the results. Rye and corn also were more or less affected by *fusarium* and other fungus diseases. In later tests the rye and corn were sterilized in dilute silver nitrate, then washed in water, in sodium chloride solution, and again rinsed. This almost entirely prevented any infection. The barley used in later tests through the courtesy of the Wisconsin Experiment Station, was given a hot-air treatment of 24 to 30 hours. This almost entirely prevented infection by *helminthosporium* and at the same time caused no injury to germination. With the later tests 2100 cc. wide-mouth jars were used and the seedlings were supported by cotton in $\frac{1}{4}$-inch holes cut with a cork borer in the edge of the wide, flat, paraffined corks. Germination was made in large jars of tap-water over which was stretched paraffined mosquito netting.

The first series of tests on rye, pop corn, and barley were grown in duplicate in Tottingham's (8) sub-optimiun solution, 480-cc. bottles were used and the nutrient changed weekly. The results of these tests are shown in table 1.

Both top and root weights are the relative total dry weights of the duplicate sets of six plants. A study of these results show that for barley as well as rye, the aluminum salts have given higher average yields than the acids. With pop corn there was a tendency for the aluminum salts to reduce the yield more than the acids did. These results are not believed to be significant, because the nutrient used was later shown not to be suited to show this point and equivalent pH values were not held in acids and aluminum salts.

If the results are averaged according to acid groups, there is little difference among the strong acids. The plants grown with sulfuric acid show slightly the lowest weights, then hydrochloric acid, nitric acid, phosphoric acid and tartaric acid follow in order. Tartaric acid tended to average higher than any of the mineral acids or their aluminum salts. A correlation of the pH values before and after growth, shows that in every case where there was a good growth of barley the hydrogen-ion concentration was markedly lowered. This change in pH value occurred in the N/4800 concentrations of the strong acids and their aluminum salts only. It occurred with the N/2400 as well as the N/4800 phosphoric acid solutions, and with all solutions of tartaric acid or aluminum tartrate. This is in accord with the results reported by Hoagland (4).

TABLE 1

Growth of rye, barley and pop corn in Tottingham's nutrient solution, May, 1919

NUMBER	TREATMENT	pH VALUE OF SOLUTION		WEIGHT OF PLANTS RELATIVE TO CHECK		
		Beginning	End	Rye	Barley	Corn
				per cent	*per cent*	*per cent*
1	Check	6.4	6.5	100	100	100
2	HNO_3 N/600	2.9	2.9	29	17	77
3	HNO_3 N/1200	3.1	3.1	41	24	53
4	HNO_3 N/2400	3.4	3.5	71	34	105
5	HNO_3 N/4800	3.6	6.3	73	65	186
6	$Al(NO_3)_3$ N/600	3.9	3.7	52	33	51
7	$Al(NO_3)_3$ N/1200	3.9	3.8	65	33	39
8	$Al(NO_3)_3$ N/2400	4.0	3.9	70	42	63
9	$Al(NO_3)_3$ N/4800	4.1	6.4	69	65	103
10	H_2SO_4 N/600	2.9	2.9	28	19	48
11	H_2SO_4 N/1200	3.1	3.1	32	25	61
12	H_2SO_4 N/2400	3.4	3.5	57	34	144
13	H_2SO_4 N/4800	3.7	6.3	97	53	136
14	$Al_2(SO_4)_3$ N/600	3.9	3.9	56	28	38
15	$Al_2(SO_4)_3$ N/1200	3.9	4.0	53	34	58
16	$Al_2(SO_4)_3$ N/2400	4.0	4.0	63	31	77
17	$Al_2(SO_4)_3$ N/4800	4.1	6.3	56	45	126
18	HCl N/600	2.9	2.9	20	21	41
19	HCl N/1200	3.1	3.1	29	23	70
20	HCl N/2400	3.4	3.5	61	35	85
21	HCl N/4800	3.7	6.4	78	63	93
22	$AlCL_3$ N/600	3.8	3.8	54	34	49
23	$AlCL_3$ N/1200	3.9	3.9	84	37	55
24	$AlCL_3$ N/2400	3.9	4.0	81	42	49
25	$AlCL_3$ N/4800	4.0	6.7	57	69	79
26	Tartaric Acid N/600	3.1	5.9	29	29	42
27	Tartaric Acid N/1200	3.4	6.4	61	42	60
28	Tartaric Acid N/2400	3.5	6.4	101	77	77
29	Tartaric Acid N/4800	3.8	6.5	132	87	115
30	Aluminum Tartrate N/600	3.9	6.5	96	43	110
31	Aluminum Tartrate N/1200	4.1	6.8	91	75	107
32	Aluminum Tartrate N/2400	4.1	6.5	74	92	239
33	Aluminum Tartrate N/4800	4.2	6.5	72	89	92
34	$Al_2(SO_4)_3$ N/600 + H_3PO_4 N/600	3.0	4.1	32	24	44
35	$Al_2(SO_4)_3$ N/600 + $CaH_4(PO_4)_2$ N/600	3.3	3.4	48	27	54
36	$Al_2(SO_4)_3$ N/600 + $Ca_2H_2(PO_4)_2$ N/600	3.6	3.6	53	33	86
37	$Al_2(SO_4)_3$ N/600 + $Ca_3(PO_4)_2$ N/600	4.0	5.3	56	56	119

TABLE 1—*Concluded*

NUMBER	TREATMENT	pH VALUE OF SOLUTION		WEIGHT OF PLANTS RELATIVE TO CHECK		
		Beginning	End	Rye	Barley	Corn
				per cent	*per cent*	*per cent*
38	$Al_2(SO_4)_3$ N 600 + H_2SiO_3 N /600	3.8	3.8	77	26	52
39	$Al_2(SO_4)_3$ N /600 + $CaSiO_3$ N /600	3.9	4.2	72	33	75
40	$Al_2(SO_4)_3$ N /600 + $CaCO_3$ N 600	4 3	7.0	50	55	63
41	$Al_2(SO_4)_3$ N 600 + $MgCO_3$ N /600	4.0	4.3	61	39	47
42	$Al_2(SO_4)_3$ N 600 + Dextrose 0.1 gm.	3.9	4 0	58	died	died
43	$Al_2(SO_4)_3$ N 600 + Mannit 0.1 gm.	4.0	4.1	53	died	34
44	$Al_2(SO_4)_3$ N 600 + Glycerine 0.1 gm.	4.1	4.2	52	died	40
45	$Al_2(SO_4)_3$ N 600 + Carbon Black 0.1 gm.	3.8	4.0	82	36	43
46	H_3PO_4 N 600	3.2	3.5	56	35	45
47	H_3PO_4 N 1200	3.6	4.1	45	42	98
48	H_3PO_4 N/2400	3.9	6.3	44	79	136
49	H_3PO_4 N/4800	4.2	6.4	69	86	76
50	H_2SO_4 N/600 + $CaCO_3$ N 600	3.6	6.9	none	99	200

Total dry weights of roots and tops on checks:
6 rye plants, 3 weeks old ..... 0.531 gm.
6 barley plants, 3 weeks old ..... 0.896 gm.
4 pop corn plants, 4 weeks old ..... 0.254 gm.
Hydrogen-ion concentration was taken by colorimetric method at beginning and end of test on barley.

The only supplementary treatments which caused good growth in barley were those that decreased the hydrogen-ion concentration. It should be noted, however, that calcium carbonate was of much greater benefit in reducing the toxicity of sulfuric acid than it was in correcting the aluminum sulfate injury, although it corrected the acidity in both solutions. In some of the results on corn shown in table 1, as well as in some preliminary work with barley, the nutrient checks did not show as good growth as the treatments of weaker acids and aluminum salts. This was thought to be due at least partly to lack of available iron. For the same reason the N/4800 aluminum-salt rye cultures were inferior to those containing more aluminum. In the later tests, citrate of iron was substituted for phosphate of iron with satisfactory results. These results are in accord with the work of Jones and Shive (5) and others who have found that iron is a more important ingredient in nutrient solutions than earlier investigators thought.

Plate 1 shows the relative growth of rye, pop corn, and barley with sulfuric acid and aluminum sulphate of equivalent normality. The rye roots show a greater tolerance toward aluminum salts than either pop corn or barley. The difference in top growth is not so apparent.

It was thought, from the first year's work, that it would be necessary to devise some method of holding the hydrogen-ion concentration constant, before definite conclusions could be reached. A constant flow of nutrient was tried in a tentative test without success. The flow of nutrient was regulated by Hofmann pinchcocks. This test was a failure on account of inability to secure an equal flow in all bottles. To regulate this condition 2100-cc. bottles were used and the nutrient changed daily instead of weekly.

Barley was grown in Shive's (7) R_4C_5 sub-optimum nutrient solution in the next test. Glass bottles of 2100 cc. capacity were used and the nutrient changed daily except at the end of the test when the changes in pH values of the solutions were noted. Nutrients of 0.025, 0.1, and 0.4 atmospheres osmotic pressure and sulfuric acid of four strengths were used. Table 2 shows the growth of barley nutrients of different strength and corresponding variable hydrogen-ion concentrations. Because of the buffer action of the stronger nutrients, it was necessary to use more acid to keep the pH values constant.

TABLE 2

Growth of barley in three concentrations of Shive's R_4C_5 solution, February, 1920

NUMBER	TREATMENT	pH	0.025 ATMOSPHERE			0.1 ATMOSPHERE			0.4 ATMOSPHERE		
			Normality equivalent	Total weight of 4 plants	Relative growth	Normality equivalent	Total weight of 4 plants	Relative growth	Normality equivalent	Total weight of 4 plants	Relative growth
				gm.	*per cent*		*gm.*	*per cent*		*gm.*	*per cent*
1	Check...	5.8	0	0.8667	100.0	0	1.6615	100.0	0	2.7854	100.0
2	H_2SO_4...	3.4	N/2600	0.3997	46.1	N/2400	0.7814	47.0	N/1600	1.1999	43.1
3	H_2SO_4...	3.8	N/6200	0.5335	61.6	N/4800	0.8527	51.3	N/3300	1.1659	42.0
4	H_3SO_4...	4.0	N/9000	0.5332	61.5	N/7200	1.0371	62.4	N/4100	1.4744	52.9
5	H_3SO_4...	4.2	N/12000	0.6022	69.5	N/9600	1.0118	60.9	N/4700	1.8917	67.1

The normality equivalent given in the table is the normality of a solution made with pure water and the given amount of acid. Table 2 shows that the stronger the nutrient, the greater was the growth; but that there is a somewhat closely corresponding depression in growth of treated plants as conpared with check plants. The amounts given are the total weights of four barley plants. Figure 1 shows graphically the pH values of the different nutrient solutions after 3 weeks' growth of barley. These values were determined by the colorimetric method in duplicate solutions. The two checked quite closely in all readings and the values used are the average of both determinations. The change in values took place in proportion to the size of the plants. The richer the nutrient, the greater was the pH change; also, the weaker the acidity, the greater the change.

In May and June, 1920, new series of water cultures were conducted with rye, barley and corn. Shive's R_4C_5 nutrient of 0.2 atmospheres pressure was used. Lime water was added to bring it to a pH value of 6.3. Sulfuric acid

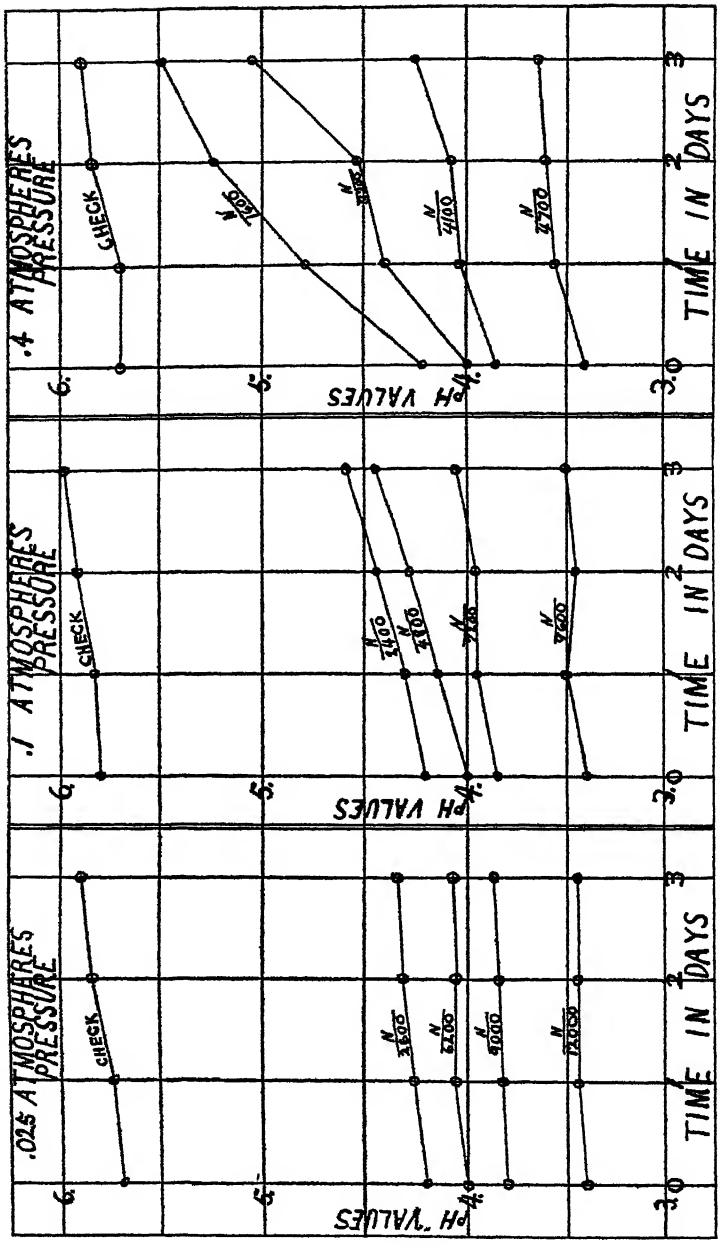

FIG. 1. CHANGE IN HYDROGEN-ION CONCENTRATION OF SHIVE'S R_4C_5 NUTRIENT SOLUTION OF VARYING STRENGTH AND ACIDITY, DUE TO GROWTH OF BARLEY IN IT

and aluminum sulfate were added to vary the pH from 3.6 to 5.7 on the acid and from 3.9 to 5.7 for the aluminum sulfate. The value pH 3.9 was taken as the strongest concentration for aluminum sulfate because it would take an excessively large quantity of aluminum sulfate to increase the concentration beyond pH 3.9. Table 3 shows the treatment, hydrogen-ion concentration of nutrient used, and the relative weights of rye, barley and yellow dent corn grown in water cultures. These results confirmed those of the previous tests, that aluminum salts on an average were less toxic than the same hydrogen-ion concentration of acid, even when the pH value was maintained by frequent changing of nutrient in large containers. The weights given are for the air-dry total roots and tops of four plants grown in duplicate jars. Shive's nutrient has a fairly large amount of phosphate in it, thus allowing for the possibility of aluminum precipitation. Plate 2 shows the growth of barley grown

TABLE 3

Growth of rye, barley and corn with constant hydrogen-ion concentration in Shive's R_4C_5 solution

NUMBER	TREATMENT	NORMALITY EQUIVALENT	pH	4 DRY RYE PLANTS, 3 WEEKS		4 DRY BARLEY PLANTS, 3 WEEKS		4 DRY CORN PLANTS, 10 DAYS	
				Total weight	Per cent of check	Total weight	Per cent of check	Total weight	Per cent of check
				gm.		*gm.*		*gm.*	
1	H_2SO_4.....	N/1800	3.6	0.5591	43	0.8647	31	1.45	78
2	H_2SO_4.....	N/3000	4.3	0.4033	31	1.6750	59	1.66	90
3	H_2SO_4.....	N/4000	5.0	0.9269	72	1.5277	54	2.29	124
4	H_2SO_4.....	N/4800	5.7	1.3241	103	2.6647	94	2.06	111
5	$Al_2(SO_4)_3$.....	N/1000	3.9	0.5416	43	0.9597	34	1.59	86
6	$Al_2(SO_4)_3$.....	N/1750	4.3	0.9155	71	1.8081	64	1.63	88
7	$Al_2(SO_4)_3$.....	N/2500	5.0	0.9671	75	2.6494	93	1.85	100
8	$Al_2(SO_4)_3$.....	N/3500	5.7	1.0857	84	2.7252	96	2.18	118
9	Check.....	0	6.3	1.2872	100	2.8363	100	1.85	100

in Shive's nutrient at the end of 3 weeks. Both roots and tops show a gradual increase in size when the hydrogen-ion concentration is lowered either in the presence of sulfuric acid or aluminum sulfate. Some difference in habit of root growth may be noted when comparing the acid with the aluminum salt.

Plate 3 shows the growth of dent corn with the treatments given in table 3. Although the nutrient was changed daily and the pH value kept constant, the corn shows an astonishingly healthy appearance at pH 3.6 in the sulfuric acid solution. It is doubtful if any natural soils ever have a pH value as low as 3.6. The results given in table 3 as well as those in table 1 show that corn has done better with a pH value around 5 than it has at 6.3 and 6.4.

In trying to correlate these results with those of Miyake (6) and Hartwell and Pember (3) it should be noted that Miyake did his work with distilled water containing no nutrients. Hartwell and Pember used a nutrient low

in phosphate, also one which they said "must not become physiologically alkaline as a result of the growth of the seedlings, for fear that the aluminum would be precipitated." To do this, they replaced part of the nitrate with an ammonium salt. A preliminary test with Hartwell and Pember's nutrient showed that there was a tendency for their nutrient not only not to become alkaline, but it actually became more acid as the plants removed ammonium

Table 4 shows the relative elementary composition of the nutrient solutions used in the various tests. The ideal nutrient for such studies remains to be worked out. Hartwell and Pember's nutrient allows for very good growth in control bottles but the ammonium ion should be reduced in proportion to the nitrate ion in order more nearly to hold the nutrient at a fixed hydrogen-ion concentration. If nutrients are changed daily or oftener and the plants grown in large containers this is not so important a factor. While Tottingham's nutrient which we used, contained approximately the same amount of phosphorus as Hartwell and Pember's nutrient, it was very much more dilute

TABLE 4

Relative composition of different nutrients

ELEMENT	TOTTINGHAM'S	SHIVE'S	HARTWELL AND PEMBER'S
	gm. per liter	*gm. per liter*	*gm. per liter*
P	0.002	0.055	0 002
N	0 008	0.042	0.070
K	0.010	0.067	0 030
Ca	0.007	0 060	0.053
Mg	0.009	0.013	0 020
S	0.012	0 018	0.026

so far as the other elements were concerned, and did not allow good growth in the check solutions.

As a further check on the question, barley and rye were grown in Hartwell and Pember's nutrient. Table 5 gives the treatment, pH values and relative whole plant weights of the barley and rye at the end of 2 weeks. The pH values were held fairly constant by daily changes of nutrient in 2100-cc. bottles. In a separate test in the small 480-cc. bottles the same nutrient with barley growing in it changed from pH 6.0 to pH 4.3 in three days. The nutrient solutions above pH 4.2 all tend to approach an equilibrium at about pH 4.2 whether containing sulfuric acid or aluminum sulfate or no added treatment. Table 5 shows that aluminum sulfate is much more toxic to barley than sulfuric acid, except at a hydrogen-ion concentration of 5.0 or above. Similar results were obtained in small bottles. Rye is more tolerant than barley toward aluminum but even rye did better with the acid than it did with the aluminum sulfate. There was no sign of aluminum precipitation with Hartwell and Pember's nutrient as there was with Shive's, yet the

nutrient seemed to contain enough phosphate for normal growth. Plate 4 shows the relative growth of barley and rye at different hydrogen-ion concentrations with sulfuric acid and aluminum sulfate in Hartwell and Pember's nutrient. Both roots and tops of barley were stunted by the aluminum salts. These last results seem to show fairly conclusively that aluminum is in itself toxic. Everything seems to indicate that phosphorus will help prevent aluminum toxicity.

Both pot and field tests at the Indiana Agricultural Experiment Station (2) bear out the contention that aluminum is in itself toxic and that with many soils and crops the presence of soluble salts of aluminum is a more important factor than is the mere hydrogen-ion concentration of the soil.

It must be granted, however, that everything else being equal, the higher the hydrogen-ion concentration, the more chance there is for aluminum to

TABLE 5

Growth of barley and rye in Hartwell and Pember's nutrient

NUMBER	TREATMENT		pH	RELATIVE WEIGHTS	
				Barley	Rye
		cc.		*per cent*	*per cent*
1	0.2*N* H_2SO_4	2.00	3.9	73	65
2	0.2*N* H_2SO_4	1.00	4.2	93	95
3	0.2*N* H_2SO_4	0.50	5.0	90	90
4	0.2*N* H_2SO_4	0.25	5.7	101	95
5	0.2*N* $Al_2(SO_4)_3$	5.00	3.9	47	55
6	0.2*N* $Al_2(SO_4)_3$	1.30	4.2	68	65
7	0.2*N* $Al_2(SO_4)_3$	0.75	5.0	91	80
8	0.2*N* $Al_2(SO_4)_3$	0.50	5.7	121	90
9	(Check)		6.3	100	100

be present in soluble form. Thus for two reasons a determination of hydrogen-ion concentration in the soil is of value in determining its productivity.

The methods involving the use of salts of strong acids, such as the Hopkins potassium nitrate method, are very valuable from a practical as well as a theoretical standpoint. They show the amount of soluble aluminum present in the soil better than other types of soil acidity methods, such as the lime-water methods, which in adition measure the less toxic acid, organic compounds in the soil.

SUMMARY

1. Water cultures of barley, rye and pop corn in Tottingham's sub-optimum nutrient solution showed approximately the same degree of toxicity with acids and aluminum salts, of equal normality.

Wherever good growth was made the hydrogen-ion concentration of the solution was decreased.

About the same toxicity was obtained with acids and aluminum salts of nitric, sulfuric and hydrochloric acids. Phosphoric acid showed less, and tartaric acid the least, toxicity.

2. With Shive's R_4C_5 nutrient at 0.025, 0.1 and 0.4 atmospheres osmotic pressure, and with varying hydrogen-ion concentration, greater growth was obtained with the stronger solutions. The ratio of growth of treated plants at the varying pH values to that of the check was approximately the same with the nutrient at all strengths.

Wherever growth was made a lowering of the hydrogen-ion concentration was noted. This was in proportion to the size of the plants.

3. Three series of cultures were made with barley, rye and dent corn in Shive's nutrient, with four corresponding degrees of hydrogen-ion concentration for sulfuric acid and for aluminum sulfate. It was found that sulfuric acid was more toxic at the same pH value than aluminum sulfate with this nutrient. More or less precipitate was noticed in the bottles containing aluminum salts.

In this test 2100-cc. containers were used and the nutrient changed daily to prevent variation in pH value.

4. Hartwell and Pember's nutrient, which contains very much less phosphorate in proportion to the other elements, was used in cultures with barley and rye at the same pH value of sulfuric acid and aluminum sulfate.

In this nutrient aluminum sulphate proved to be much more toxic to barley than did the same hydrogen-ion of sulfuric acid. Rye was slightly more injured by the aluminum salts than by the acid.

Hartwell and Pember's nutrient tends to become more acid as the plants grow.

5. It is concluded that the toxicity of aluminum salts is due to the aluminum ion more than it is to the hydrogen ion on such plants as barley and that this toxicity is reduced when much phosphate is used in the nutrient.

These results confirm the conclusions of Hartwell and Pember and Miyake.

6. Acid soils are toxic to many plants largely because they contain easily soluble aluminum salts.

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PLATE 1

ILLUSTRATIONS OF WATER CULTURES WITH VARYING STRENGTHS OF SULFURIC ACID AND ALUMINUM SULFATE; TOTTINGHAM'S NUTRIENT.

Fig. 1. Rye.
Fig. 2. Barley.
Fig. 3. Pop Corn.

S D CONNER AND O H SEARS

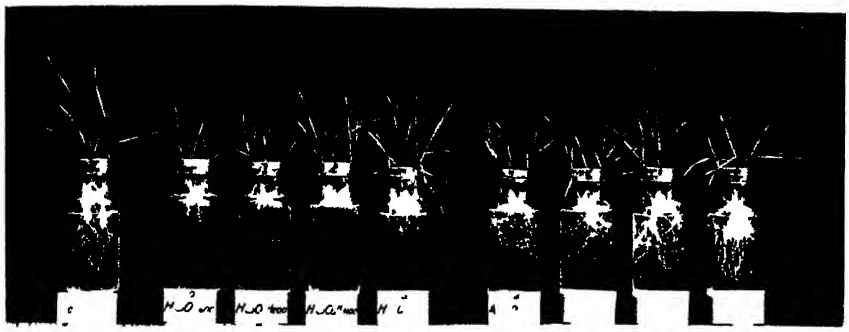


FIG 1

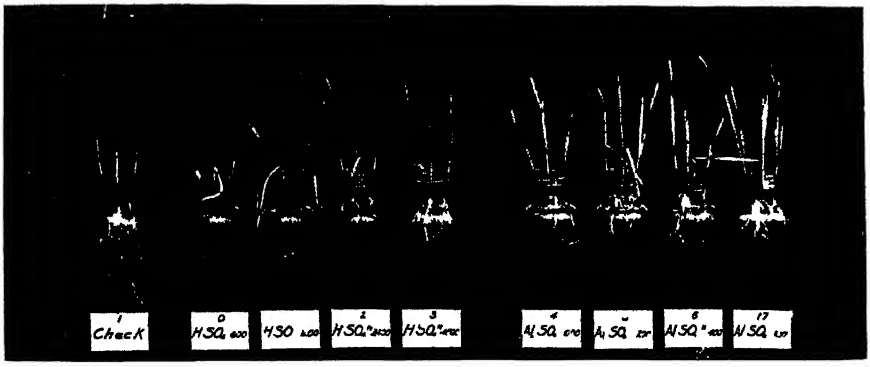


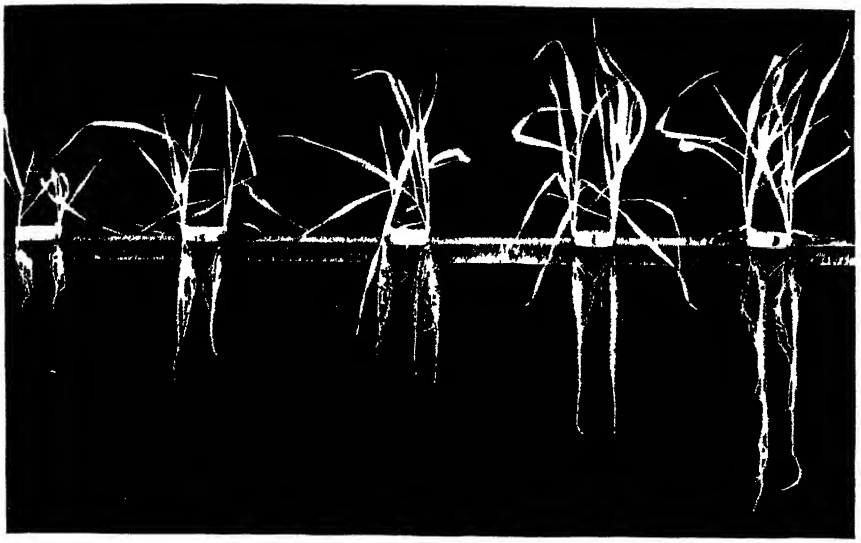
FIG. 2

FIG. 3

PLATE 2

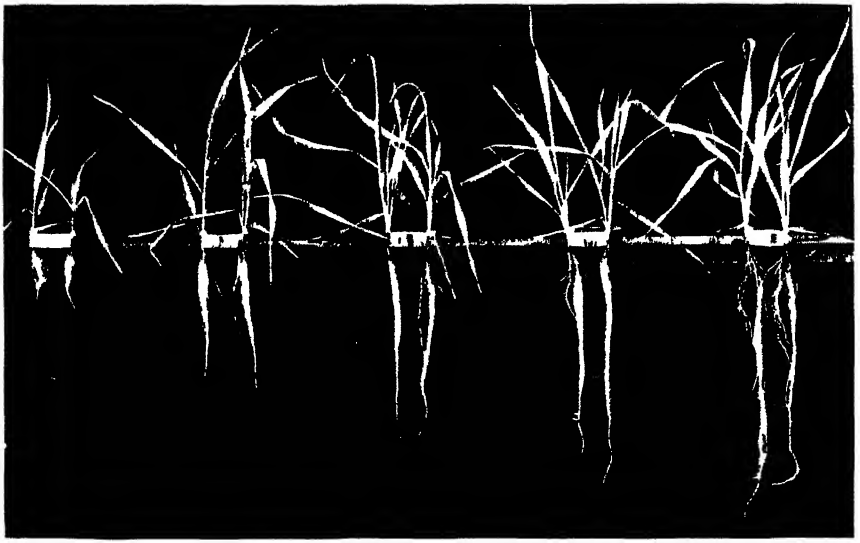
ILLUSTRATIONS OF WATER CULTURES WITH BARLEY IN SHIVE'S NUTRIENT. SEE TABLE 3 FOR TREATMENTS.

Fig. 1. Growth of barley with varying pH values of sulfuric acid. Check plants at right.
Fig. 2. Growth of barley with varying pH values of aluminum sulfate. Check plants at right.



pH 3 6 H_2SO_4 | pH 4 3 H_2SO_4 | pH 5 0 H_2SO_4 | pH 5 7 H_2SO_4 | pH 6 3 Check

FIG 1



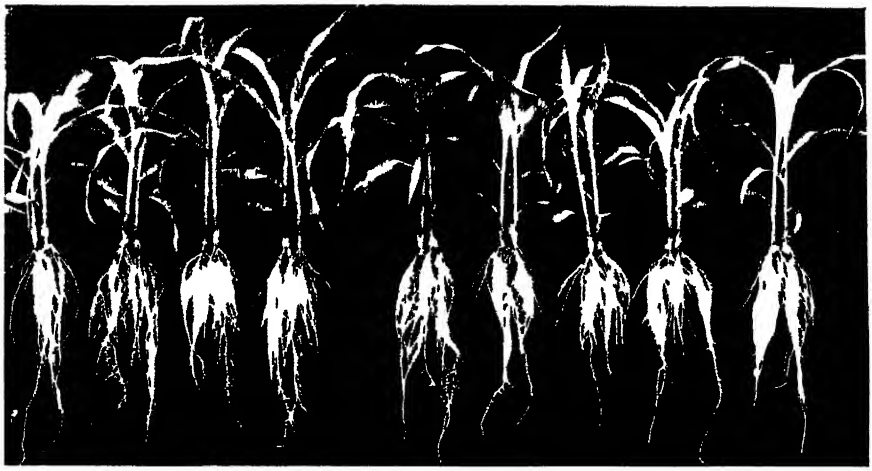
pH 3 8 $Al_2(SO_4)_3$ | pH 4 3 $Al_2(SO_4)_3$ | pH 5 0 $Al_2(SO_4)_3$ | pH 5 7 $Al_2(SO_4)_3$ | pH 6 3 Check

FIG. 2

PLATE 3

ILLUSTRATION OF WATER CULTURES WITH DENT CORN IN SHIVE'S NUTRIENT AT VARYING pH WITH H_2SO_4 AND $Al_2(SO_4)_3$. SEE TABLE 3 FOR TREATMENTS, CHECK AT RIGHT.

S D CONNER AND O H SEARS

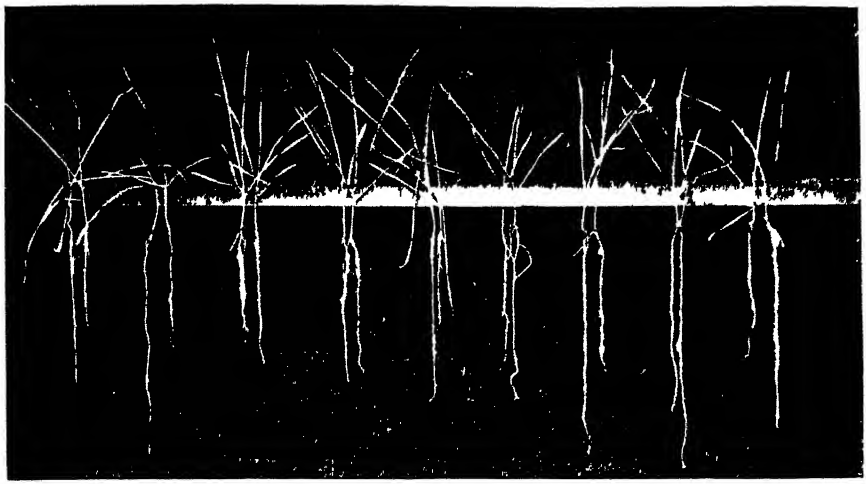


pH 3 6	pH 4 3	pH 5 0	pH 5 7	pH 3 8	pH 4 3	pH 5 0	pH 5 7	pH 6 3
H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	Check

PLATE 4

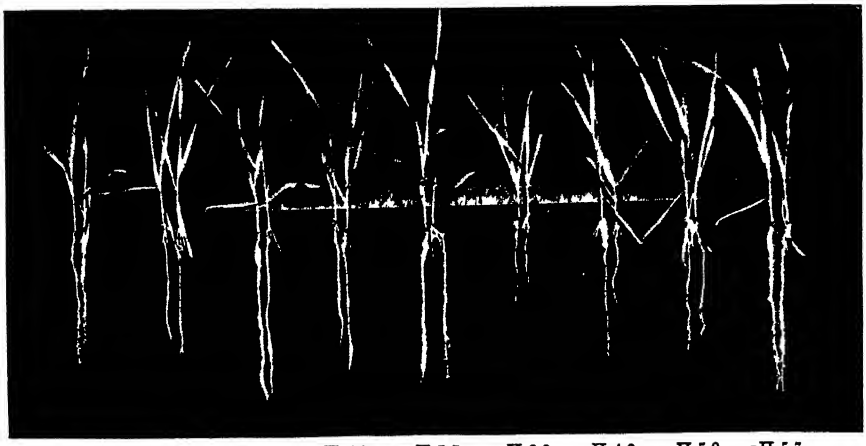
ILLUSTRATIONS OF WATER CULTURES IN HARTWELL AND PEMBER'S NUTRIENT. SEE TABLE 5 FOR TREATMENTS, CHECK AT LEFT; OTHERWISE NUMBERED FROM LEFT TO RIGHT.

Fig. 1. Rye.
Fig. 2. Barley.



pH 6 3 check | pH 3 9 H_2SO_4 | pH 4 2 H_2SO_4 | pH 5 0 H_2SO_4 | pH 5 7 H_2SO_4 | pH 3 9 $Al_2(SO_4)_3$ | pH 4 2 $Al_2(SO_4)_3$ | pH 5 0 $Al_2(SO_4)_3$ | pH 5 7 $Al_2(SO_4)_3$

FIG. 1



pH 6 3 Check | pH 3 9 H_2SO_4 | pH 4 2 H_2SO_4 | pH 5 0 H_2SO_4 | pH 5 7 H_2SO_4 | pH 3 9 $Al_2(SO_4)_3$ | pH 4 2 $Al_2(SO_4)_3$ | pH 5 0 $Al_2(SO_4)_3$ | pH 5 7 $Al_2(SO_4)_3$

FIG. 2

THE CLASSIFICATION OF SOIL MOISTURE[1]

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INTRODUCTION

The soil moisture is generally classified into three forms; namely, hygroscopic, capillary, and gravitational water. This classification is based upon the vapor pressure exerted by the soil water and upon the water-holding capacity of the soil. This is the classification given in most texts on the subject and it is very satisfactory for many purposes.

A new classification of the soil moisture, based upon results obtained with the freezing-point and dilatometer methods, has been offered by Bouyoucos (3). The freezing-point lowering of a soil was found by Bouyoucos and McCool (4) to increase in approximately geometric progression as the moisture content decreased in arithmetric progression. This indicated that, contrary to the general belief, the concentration of the soil solution is not inversely proportional to the moisture content of the soil. The hypothesis, which was advanced to explain the results, assumes that the soil renders part of the soil water inactive as a solvent, thereby causing the soil solution to be more concentrated than is indicated by the percentage of moisture in the soil. The amount of this inactive or unfree water could not be measured satisfactorily by the freezing-point method so the dilatometer method was selected for this purpose. This method depends upon the principle that water expands on freezing and the amount of water frozen is indicated by the amount of expansion. Bouyoucos (3), using this method has classified the soil water as follows:

- Gravitational
- Free
- Unfree
  - Capillary-adsorbed
  - Combined
    - water of solid solution or
    - water of hydration

[1] Part 2 of a thesis submitted at the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Prof. E. Truog.

The free water is that which will freeze the first time it is cooled to −1.5°C. The capillary-adsorbed water is the additional amount that can be frozen at lower temperatures. The combined water is that which cannot be frozen. The lowest temperature used was −78°C.

The properties attributed to the different forms of water in this new classification are very distinct. The free water[2] is considered as the only form acting as a solvent for the salts in the soil. A part of the capillary-adsorbed water is rendered free by successive freezing and thawing and then acts as a solvent. The combined water is supposed to exist as water of solid solution or as water of hydration and therefore is not a solvent. It is also considered that the free water is readily available to plants, that the capillary-adsorbed water is only slightly available, and that the combined water cannot be utilized by plants. Bouyoucos (3) also states that the free water would possess one velocity of evaporation, the capillary-adsorbed another, and the combined water still another. Thus it is seen that this investigator has given an entirely new conception of the moisture relations of the soil and the forms of water in the soil.

The dilatometer method has been used in studying the forms of water in hydrogels, and this has resulted, as in soils, in a conception different from that generally held, as to the forms of water present. Since the vapor-pressure and dilatometer methods have led to different conceptions as to the forms of water in both soils and hydrogels, it seems possible that one of the methods may be influenced by factors which have not been recognized. It is the purpose, therefore, of the present paper to review some of the work of previous investigators on the forms of water in hydrogels and soils, and to present some new data which indicate that all of the soil water acts as a solvent. The terms soil water or soil moisture are understood by the writer to include only that water which is lost from a soil by drying in an oven at 105°C. for 12 hours. No doubt soils contain more water, some of which is chemically combined, that would be lost on ignition. The moisture in hydrogels is expressed as total moisture on the wet basis, determined by ignition to constant weight.

HISTORICAL

Van Bemmelen (17, 18) studied the forms of water in hydrogels by determining the vapor pressure of the gel during dehydration and hydration. Dehydration curves for silica gels were obtained which had two transition points and a portion of the curve was nearly horizontal. This indicated a possible hydrate of silica. However van Bemmelen showed that the transition points do not represent definite hydrates since the water content at which

[2] In this paper the terms free water, unfree water, capillary-adsorbed water, and combined water are used with the meanings attached to them by Bouyoucos (1, 2, 3).

they occur varies widely, depending on the manner of preparation, age of the gel, and the temperature of dehydration. These characteristic points are explained by the structure of the gel. His results seemingly prove that the water is not in the form of hydrates but is absorbed. The fact that the water may be readily replaced by other liquids such as alcohol, glycerin, acetic acid, nitric acid, and concentrated sulfuric acid confirms the conclusion that the water in the hydrogel is not chemically combined.

Zsigmondy and his associates (20–22) performed similar experiments. With an improved apparatus they determined the vapor pressure of gels during dehydration and obtained results very similar to van Bemmelen's. The vapor pressure of alcogels and bensolgels was also determined and the vapor pressure curves were found to be similar to that obtained with hydrogels. All of this work indicates that the water, alcohol, benzene, or other liquid in the gel is not chemically combined with the solid but is absorbed and held in the capillary spaces of the gel.

The dilatometer method as a means of studying the forms of water in hydrogels has been used by Foote and Saxton (7, 9). They classified the water in gels into two forms, capillary and combined. The capillary water is that which will not freeze at 0°C. but can be frozen at lower temperatures. They determined the apparent capillary water, i.e., water which can be frozen only at temperatures below −6°C. The lowest temperature used was −78°C. The combined water is that which cannot be frozen. They have shown that the amount of water which cannot be frozen depends somewhat on the treatment of the gel after formation. The percentage of combined, or unfrozen, water was reduced to the lowest value by digesting the gel on the steam bath with a large amount of water. With alumina they obtained values of from 36.03 to 38.08 for the percentage of combined water. With ferric hydroxide the percentage of combined water varied from 5.42 to 21.96 depending upon the length of time the gel was digested on the steam bath. The percentage for silica gels varied from 22.87 to 30.6. Thus it is evident that a considerable but variable amount of water will not freeze at the temperature of −78°C. The results obtained for combined water by this method will obviously depend on freezing all of the capillary water. It seems possible that part of this water cannot be frozen and therefore the dilatometer method would classify some of it as combined water.

Vanzetti (19) studied the behavior of silica gels at low temperatures, using liquid air in some of his work. He prepared silica gels from silicate solutions of varying concentrations, subjected the gels to low temperatures and determined the ratio of water to SiO_2 in the gel. The ratio was found to vary from 2.25 in the gel formed from a 1 per cent SiO_2 solution to 0.72 in the gel formed from a 7 per cent solution. He concluded that the water was not chemically combined and that the absorption theory of van Bemmelen and the theory of the structure of gels account for all of the results obtained.

The effect of pressure on the water content of silica gels was determined by Lenher (12). When subjected to a pressure of 230 kgm. to the square inch the gel retained 77 per cent of water. Higher pressures reduced the water content. With a pressure of 272,000 kgm. to the square inch the water content was reduced to 12.5 per cent. This is approximately one-half the value obtained by Foote and Saxton for the combined water in silica gels. This and the other work cited indicate that the dilatometer method does not give a measure of the combined water in hydrogels and therefore it would not be expected to measure the combined water in soils.

Patten and Gallagher (15) have given a review of the literature on absorption, evaporation, and vapor pressure studies made with soils so it will only be necessary to consider the more recent investigations in this paper. Cameron and Gallagher (6) studied the rate of evaporation of water from soils over 95 per cent sulfuric acid and found that the rate of evaporation is nearly constant until the optimum moisture content of the soil is reached. From this point the rate gradually decreases and gives, when plotted, an even curve which indicates that there is no change in the physical state of the soil water. Patten and Gallagher (15) determined the vapor pressure of several soils at different moisture contents by placing the dry soils in desiccators over sulfuric acid of varying concentrations and obtained a uniform vapor pressure curve. These investigators have also determined the rate of absorption of water vapor by soils in atmospheres of different humidity. In every instance very regular rate curves were obtained, indicating that there is no abrupt change in the form of water in the soil as the moisture content is reduced from a high to a very low percentage.

Keen (10) used an improved method for studying the rate of evaporation of water from soils. A very thin layer of soil was placed in a wire basket so evaporation could take place from the top and bottom of the soil layer. This evaporation cell was placed over sulfuric acid of the desired concentration and the whole kept at constant temperature. The apparatus was so arranged that weighings could be made at frequent intervals without removing the soil from the desiccator. A similar apparatus has been used by the writer with satisfactory results. The results obtained by Keen show that the rate of evaporation decreases with the moisture content, and the conclusion is made that since there are no sharp breaks in the evaporation curve, there is no change in the physical state of the water as the moisture content is reduced. This conclusion was reasserted by Keen (11) after making a critical study of the data of Bouyoucos and McCool on the freezing-point lowering of soils.

Shull (16) measured the surface forces in soils by determining the moisture content at which Xanthium seed could no longer take up water from the soil, and the points of equilibrium between the seed and soil at different moisture contents. These results were compared with similar data in which the seed

was placed in salt solutions of known osmotic pressures. The seed reduced the moisture content of the soil to an air-dry condition and at this point the soil held the water with a force equal to about 1000 atmospheres. It is important to note that the seed was able to reduce the moisture content of the soil much below that of the unfree and even of the combined water content as would be indicated by the dilatometer method.

In studies on the displacement and freezing-point methods for determining the concentration of the soil solution, the writer (14) obtained results which indicate that the displaced solution is representative of all the water in the soil. The results also indicate that the soil does not cause a considerable amount of water to be removed from the role of a solvent. The writer (13) has also shown that solid material causes a freezing-point depression of a liquid in the film or capillary condition, and that after a certain moisture content is reached a small reduction in the amount of liquid present causes a great increase in the freezing-point depression of the liquid. These results indicate that as the moisture content is reduced a point is reached at which the water in the soil cannot be frozen on account of the great attraction between the soil and the water which is left and not because the water is no longer in the liquid state. It seems probable that the dilatometer method is a means of determining this point rather than the amount of combined water present.

Studies have been continued to determine whether or not all of the water in a soil acts as a solvent. If it does, further evidence is offered that the water is not combined but is held in the liquid state by the soil particles. The rate of evaporation of water from soils has also been determined and the results obtained agree with those of Keen so it does not seem necessary to include them here.

EXPERIMENTAL

If it is assumed that water is rendered unfree by a soil, then when a solution is added to a dry soil it would become more concentrated since part of the water would be withdrawn from the role of a solvent. It is possible to test this experimentally by both the displacement and freezing-point methods. In order to test this hypothesis by the displacement method, portions of four oven-dried soils were moistened with water, other portions were moistened with an alcohol solution, and still other portions with a glycerin solution. Each soil was brought to about its optimum moisture content with water and the two solutions. Alcohol and glycerin solutions were used because there is little probability of their reacting more than slightly with the material in the soil. The alcohol solution contained about 6 cc. of alcohol in 2000 cc. of water and the glycerin solution contained about 30 cc. of glycerin in 2000

cc. of water. The former solution gave a freezing-point depression of 0.090° and the latter a depression of 0.295°. After moistening, the soil solution was displaced from each portion and the freezing-point depression of the displaced solution determined. If water is not rendered unfree the freezing-point depression of the displaced alcohol solution should be 0.090° greater than that of the displaced water solution. Likewise the freezing-point depression of the displaced glycerin solution should be 0.295° greater. The experimental increase in the freezing-point depressions due to alcohol and glycerin are given in columns 5 and 7 of table 1.

There are two factors, adsorption and the difference in the nature of the solvent, which may affect the results obtained by both the displacement method and the freezing-point method. However the results obtained indicate that there is very little adsorption of either alcohol or glycerin. The

TABLE 1

The freezing-point depression (f. p. d.) of solutions displaced from soils, moistened as indicated, and the calculated depressions due to alcohol and glycerin; theoretical depression due to alcohol is 0.090° and to glycerin is 0.295°

SOIL	MOISTURE	MOISTENED WITH WATER	MOISTENED WITH ALCOHOL SOLUTION		MOISTENED WITH GLYCERIN SOLUTION	
		F. P. D. of displaced solution	F. P. D. of displaced solution	F. P. D. due to alcohol	F. P. D. of displaced solution	F. P. D. due to glycerin
	per cent	°C.	°C.	°C.	C.	°C.
Silt loam.....	25.0	0.055	0.138	0 083	0.348	0 293
Sand.....	15.0	0.050	0.125	0.075	0.335	0.285
Peat.....	225.0	0.116	0.198	0.082	0.405	0.289
Clay loam.....	30.0	0.051	0.140	0.089	0.355	0.304

total salts in the displaced solutions were determined in some cases and it was found that the amount of salts dissolved by the two solutions was very nearly the same as the amount dissolved by water. The agreement between the experimental and theoretical values is, in most cases, within the limit of experimental error.

The results indicate that water is not rendered unfree by a soil, as is shown by the following consideration. The silt loam soil contains 10.2 per cent of unfree water as determined by the dilatometer method. Therefore, at a moisture content of 25 per cent, 40 per cent of the water would be unfree. Assuming that this amount of water was withdrawn from the role of a solvent the freezing-point depression of the displaced alcohol solution would have been 0.193° instead of 0.138° and the depression due to the alcohol would have been 0.138° instead of 0.083°. Similar calculations for the glycerin show that the depression of the solution would have been 0.488° instead of 0.348° and the

depression due to glycerin would have been 0.433° instead of 0.293°. Therefore the experiment offers very good proof that all the soil water acts as a solvent.

The hypothesis was tested in a similar manner by the freezing-point method. Samples of the silt loam soil were brought to definite moisture contents with water. Other samples were brought to the same content with the same alcohol and glycerin solutions that were used in the preceding experiment. The freezing-point depression of all samples was determined in the usual manner. The depression obtained when the soil is moistened with water is due to the solid material and the salts in the soil solution. If water is not rendered unfree the freezing-point depression of the alcohol and glycerin solutions in the soil should be 0.090° and 0.295° greater respectively than the depression of the water in the soil. The values obtained for the depressions due to alcohol and glycerin are given in columns 4 and 6 of table 2.

TABLE 2

The freezing-point depression (f. p. d.) of water, an alcohol solution, and a glycerin solution in a silt loam soil at different moisture contents, and the calculated depressions due to the alcohol and glycerin; the theoretical depression due to alcohol is 0.090° and to glycerin is 0.295°

MOISTURE CONTENT OF SOIL	F. P. D. WATER	F. P. D. ALCOHOL SOLUTION	F. P. D. DUE TO ALCOHOL	F. P. D. GLYCERIN SOLUTION	F. P. D. DUE TO GLYCERIN
per cent	°C.	°C.	°C.	°C.	°C.
10.0	1.310	1.420	0.110	1.580	0.270
15.0	0.275	0 375	0.100	0.585	0.310
20.0	0.132	0.228	0 096	0.446	0.313
25.0	0.079	0.169	0.090	0.395	0.316
35.0	0.051	0.139	0.088	0.350	0.299
50.0	0.028	0.119	0.091	0.317	0.289

These results afford further proof that the soil does not withdraw part of the role of a solvent. If such were the case the alcohol and glycerin solutions would have been greatly concentrated at the lower moisture contents and in these cases the freezing-point depression due to alcohol and glycerin would have been many times the experimental values. Similar results have been reported (14) for a case in which a sugar solution was used with aluminium oxide.

DISCUSSION

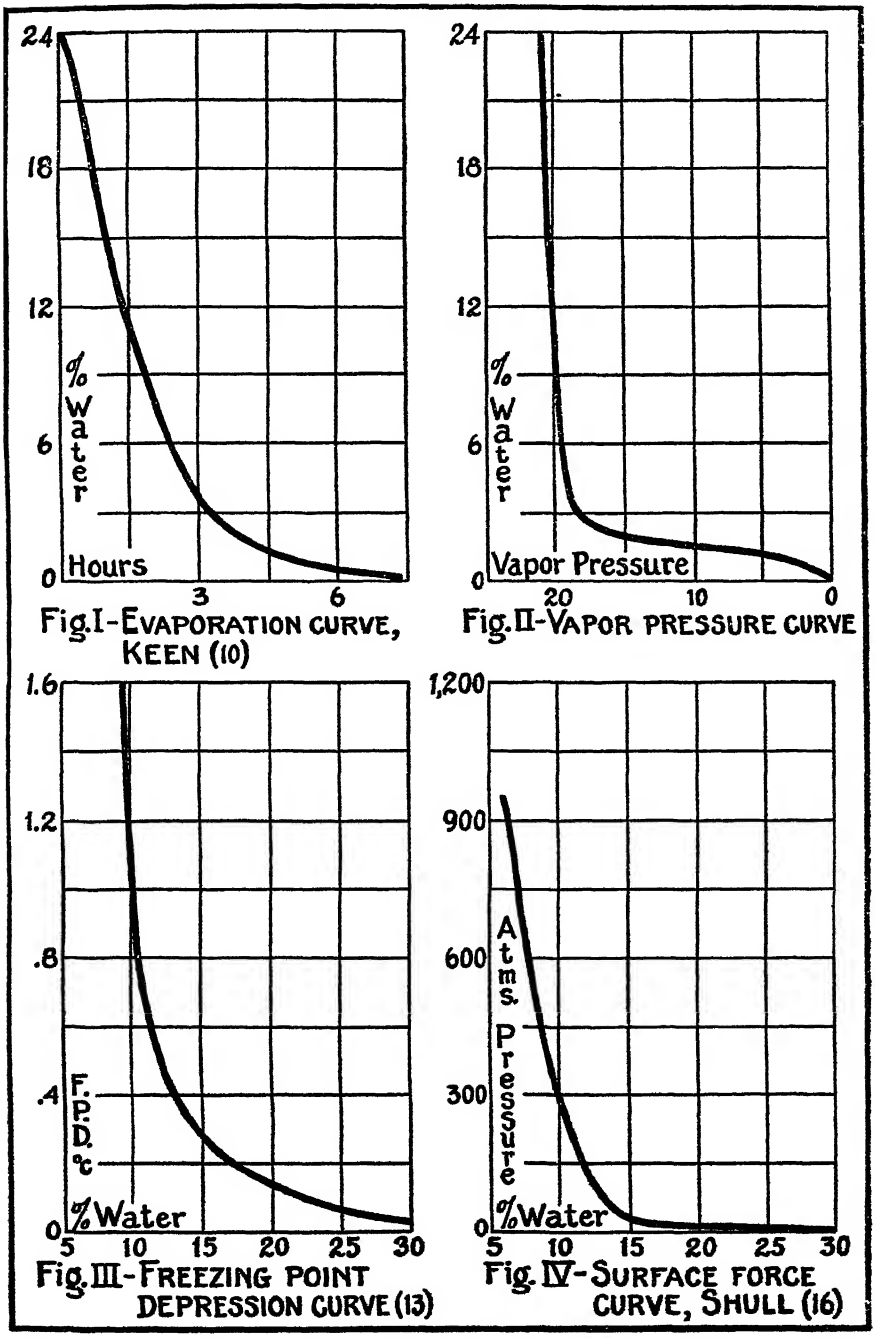
The results that have been obtained show that the soil does not render water inactive as a solvent. The water therefore must remain in the liquid state and does not become combined with any of the materials in the soil. There must, however, be a very great force holding the water to the soil. This force is sufficient to cause the vapor pressure of the soil water to be

greatly lowered at the lower moisture contents, to prevent considerable quantities of the water from freezing, to render part of the water unavailable to plants, and cause a considerable freezing-point depression of the soil water even at relatively high moisture contents. There are several methods by which this force may be measured or its relative value at different moisture contents indicated. Four methods which have been used are, (a) rate of evaporation, (b) freezing-point depression at different moisture contents, (c) vapor pressure during dehydration, and (d) equilibrium relations of the soil with seed of known water absorbing power. These methods of studying the force with which the water is held by the soil should give similar results.

In order to compare the results which have been obtained by the four methods, figures 1, 2, 3, and 4 are given. Figure 1 is the rate of evaporation of water from Hoos field soil (dunged plot) desiccated over 95 per cent sulfuric acid, as determined by Keen (10). Figure 2 is the vapor pressure curve of Superior clay, determined by the writer as follows. Samples of moist soil equal to 5 gm. of oven-dry soil were placed in 10 desiccators containing sulfuric acid of different concentrations thus giving different vapor pressures. The desiccators were kept at a constant temperature of 26°C. for 25 days after which time the moisture content of the soil was determined. Figure 3 is the freezing-point depression curve, previously given (13), for Carrington silt loam. Figure 4 is the curve obtained by Shull (16) for the subsoil of Oswego silt loam. Shull's measurements were made by determining the points of equilibrium between the soil and Xanthium seed of known water-absorbing power. Each method was used with a different soil but in all cases it was a fairly heavy type.

The curve obtained by the four methods are very similar. This would be expected since they are all graphic representations of the force with which water is held by the soil at different moisture contents. The main difference in the different curves is that the point of greatest curvature comes at different moisture contents. This is undoubtedly due for the most part to the difference in the sensitiveness of the methods. An increase in the force which could hardly be detected by vapor-pressure methods is readily shown by an increase in the freezing point depression. The freezing-point method and probably the method of Shull are more sensitive than the evaporation or vapor-pressure methods. Therefore the point of greatest curvature in the curve obtained by the former methods will be at higher moisture contents than the corresponding points obtained by the latter methods. All of these methods indicate that the water at low moisture contents is held with a much greater force than the additional water at the high moisture contents.

The dilatometer method of determining the forms of water in a soil probably only indicates the moisture contents at which this attractive force for the remaining water has certain values. The supposed unfree water content



FIGS. 1, 2, 3 AND 4. CURVES SHOWING THE SIMILARITY OF RESULTS OBTAINED BY FOUR METHODS OF STUDYING THE FORCE WITH WHICH SOILS HOLD WATER

of a soil is probably very nearly that moisture content at which the force is great enough to produce a freezing-point depression of 1.5°C. The combined water content is that moisture content at which the attraction between the soil and the water is so great that the water cannot be frozen. The percentage of water which does not freeze the first time at −1.5° is of particular interest for, as has been shown by Bouyoucos (1), it approximates very closely the wilting point of the soil, The moisture equivalent, wilting point, hygroscopic coefficient, water-holding capacity, and unfree water content are all measures of the attractive force the soil has for water. Briggs and Shantz (5) have shown, for all but the unfree water, that there is a rather definite relation between them. The writer (14) has shown that at the moisture equivalent the freezing-point depression of the soil water due to the solid material is very nearly a constant. It is very probable that at the wilting coefficient the freezing-point depression would be practically a constant for all soils. The combined water, as determined by the dilatometer method, would not bear any definite relation to these points for in determining the combined water the soil is subjected to freezing and thawing which greatly alters its physical properties.

The amount of water held by a soil with a given force is determined very largely by its colloidal material. Any treatment which alters the soil colloids will affect the amount of water held by the soil with a given force. This has been shown by Bouyoucos and McCool (4) with the freezing-point method. Successive freezing and thawing or ignition, by destroying some of the colloidal properties of heavy soils greatly reduces the freezing-point depression due to solid material at a given moisture content. Keen (10) has shown that water evaporates much faster from a soil in which the colloids have been destroyed by ignition than from the same soil which has not been ignited. Therefore it is evident that the soil colloids are very important in considering the moisture relations of the soil.

SUMMARY

In order to explain results obtained in a study of the freezing-point lowering of soils at different moisture contents, Bouyoucos and McCool (4) advanced the hypothesis that a portion of the soil water is inactive or unfree, that is, does not act as a solvent. The dilatometer method was later used to measure quantitatively the unfree water of the soil, and based upon that method Bouyoucos (3) has offered a new classification of the soil moisture. The most striking feature of the new classification is the unfree water, that is, the water which is not supposed to act as a solvent although it may be present in considerable amounts. Bouyoucos reports that the percentage of this form of water in soils varies from 1.2 in a coarse sand to 22.84 in a clay.

Evidence presented in this and previous papers (13, 14) shows that the dilatometer method does not measure different forms of water in the soil, and

that soils do not contain a considerable percentage of water which does not act as a solvent. This evidence is summarized as follows:

1. The much greater increase in the freezing-point depression of soils with a decrease in the moisture content than is indicated by the law of inverse proportion, is due to the solid material and not to the existence of unfree water which would cause a greater concentration of the soil solution. It has been shown that solid material causes a depression of the freezing-point of water, benzene, and nitrobenzene in the film or capillary condition.

2. Alcohol and glycerin solutions are not made more concentrated when added to a dry soil, as would be the case if part of the water was rendered unfree by the soil. Therefore all of the soil water must act as a solvent and exist in the liquid condition.

3. It is possible to displace part of the soil solution from a soil whose moisture content is less than that of the unfree water.

4. A number of investigators have shown that the water of certain inorganic hydrogels is not combined water. However, these hydrogels contain a considerable amount of water which cannot be frozen and a still larger amount which would be classified as unfree water under the new classification.

5. Studies on the rate of evaporation of water from soils, the vapor pressure at different moisture contents, the equilibrium relations with seeds, and the freezing-point depression due to solid material do not indicate the presence of different forms of soil water such as are given in the dilatometer classification.

All of the results obtained are readily explained as follows. At moisture contents below the water-holding capacity of the soil the water is held to the soil by an attractive force commonly called adhesion. As the moisture content of the soil gradually decreases the force with which the remaining water is held continually increases. This causes an increase in the freezing-point depression of the soil water, a decrease in the rate of evaporation, and a decrease in the vapor pressure of the soil water as the moisture content is reduced. This force is great enough to prevent part of the soil water from being frozen at very low temperatures.

The same general conclusion concerning the moisture relations of soils, as drawn by Keen (11) from his investigation of the rate of evaporation of water from the soil, and from a study of the freezing-point data of Bouyoucos and McCool, follows:

> The water present is subjected to the same law over the whole experimental range and the various constant and critical points shown by soil at varying degrees of water content, are approximate equilibrium values only and do not indicate any break or abrupt change in the physical condition of the soil moisture.

The old classification of the soil moisture into hygroscopic, capillary, and gravitational water has certain objectional features but seems to be the best

classification yet offered for most purposes. It is at least very useful in many respects.

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FERROUS SULFATE TREATMENT OF SOIL AS INFLUENCING THE SOIL SOLUTION OBTAINED BY THE LIPMAN PRESSURE METHOD

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In connection with studies conducted by the writer during the past five years on chlorosis of citrus trees, some interesting evidences of the utility of his pressure method (1) for obtaining the soil solution were adduced. While some of the results are fragmentary, I consider them interesting enough to present to those who are working on problems either of the soil solution or of chlorosis, or of both.

The soil involved in these experiments was that of a young lemon orchard in southern California in which the trees were affected by a type of chlorosis common under certain circumstances. Among other attempts to cure the diseased trees, $FeSO_4$ was applied to the soil in which they were growing. From 5 to 10 pounds of commercial $FeSO_4$ was used per tree. It was applied in a dilute solution over an area represented by a circle 15 feet in diameter with the tree trunk for center. Control trees were included in the experiment which received the same amount of water as the $FeSO_4$ treated trees, but no other treatment. After some weeks a composite soil sample of several borings was made respectively from a treated and from a control tree. The soil was sampled to a depth of 12 inches.

When the samples were received in the laboratory, they were thoroughly mixed, made up to approximately optimum moisture content and allowed to stand in tightly stoppered containers for one day. At the end of that time, they were submitted to pressure in the apparatus described in the paper cited above. The solutions thus obtained were analyzed for total solids, non-volatile solids, calcium, potassium and phosphorous. Table 1 gives the results obtained in the analyses.

TABLE 1

Analyses of 25 cc. of extract representing 125 grams of soil

TREATMENT	TOTAL SOLIDS	NON-VOLATILE SOLIDS	Ca	K	P
	grams	*grams*	*grams*	*grams*	*grams*
FSO_4.....	0.0585	0.0420	0.0044	0.0049	0.0027
Untreated.....	0.0431	0.0266	0.0023	0.0034	0.0018

The foregoing data show perfectly clearly the effectiveness of ferrous sulfate as a modifier of the composition of the soil solution. It appears to increase markedly the content of non-volatile solids in the soil solution and to precipitate the dissolved organic matter therein. The iron evidently substitutes itself readily for the common bases, calcium and potassium, and for some reason seems, besides, to bring more phosphorus into solution. Other unpublished data in my possession prove conclusively that $FeSO_4$ treatment of soil results in bringing added amounts of calcium and potassium into the soil solution. The study here described was carried out before we had become fully impressed with the profound significance of soil variability and its relations with soil sampling regarding which this laboratory was the first to make important contributions. For that reason, no control of variability was included in obtaining the data given above. Nevertheless, the effects are so uniformly consistent in one direction and so well supported by other data as above stated, that a note with regard to them seems eminently desirable.

I wish particularly to call attention to the evidence furnished in table 1 of the utility of my pressure method for obtaining the solution since I have not heretofore had an opportunity of giving actual data of analyses based thereon. Other and much fuller evidence along that line will soon be published by myself and by others.

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THE MOVEMENT OF SATURATED WATER VAPOR THROUGH QUARTZ FLOUR

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Water may move through the soil in either the liquid or vapor state. The liquid movement is of the greatest importance, especially when the soil has a comparatively high moisture content and when it is compacted to such an extent that the films between the soil grains may form a continuous liquid path through the soil. It is a common farm practice to work up the surface of the soil into a mulch to prevent this liquid movement, but the mulch will not prevent the gaseous water from diffusing up through the soil. The gaseous movement is extremely small in comparison with the liquid movement. Patten and Gallagher (1) have determined the rate of adsorption and evaporation of water in quartz flour in atmospheres of different degrees of humidity and were able to approach the equilibrium point starting with both dry and wet soil. They also showed that the adsorption of water vapor decreases with increase in temperature. This investigation is an attempt to get more definite knowledge of the nature of water vapor movement.

Consider a tube full of soil with one end closed and the other exposed to saturated water vapor. The quantity of water in the soil may be expressed by the following definite integral:

$$q = \int_a^b (\rho + c)\, dx$$

where q is the total quantity of water in the soil, ρ is the "density" of the liquid phase, c is the "density" of the gaseous phase, and x is the distance from an appropriate origin. Assume that $\rho\ (c_0 - c) =$ a constant K_1, where c_0 is the density of saturated water vapor. This assumption is based on an investigation which is being conducted at this station by Thomas. (3)

Substituting

$$q = \int_a^b \left(\frac{K_1}{c_0 - c} + c\right) dx$$

[1] The author feels much indebted to Dr. Willard Gardner for assistance in the mathematical development and to Prof. M. D. Thomas for many helpful suggestions in the laboratory technique.

Differentiating with respect to the time

$$\frac{dq}{dt} = \int_a^b \left[\frac{K_1}{(c_o - c)^2} + 1\right]\frac{dc}{dt}\,dx \tag{2}$$

Assume, as Patten and Waggaman (2) have done, that

$$\frac{dc}{dt} = K_3\,(c_0 - c) \tag{3}$$

In any length of soil tube when a state of steady flow is reached, assume that the vapor density is a linear function of x, that is, $c_o = c - K_2x$. Substituting for c and $\frac{dc}{dt}$ in (2)

$$\frac{dq}{dt} = \int_a^b \left(\frac{K_1}{(K_2\,x)^2} + 1\right) K_2K_3\,x\,dx \tag{4}$$

Integrating,

$$\frac{dq}{dt} = \frac{K_2K_3}{2}\,x^2\,\Big]_a^b + \frac{K_1K_3}{K_2}\log x\,\Big]_a^b \tag{5}$$

The integral becomes indeterminate when integrated between 0 and h, for the second term becomes $-\infty$ when the lower limit is substituted. To avoid this, integrate between $+1$ and h.

This gives

$$\frac{dq}{dt} = \frac{K_2K_3}{2}\,h^2 + \frac{K_1K_3}{K_2}\log h - \frac{K_2K_3}{2} \tag{6}$$

Putting

$$K_2K_3 \quad A \text{ and } \frac{K_1K_3}{K_2} = B, \frac{dq}{dt} = Ah^2 + B\log h - A \tag{7}$$

The following experimental method was used to test the accuracy of this equation. Finely ground quartz flour was placed in weighing bottles in different quantities so that when the bottles were tapped until the flour would settle no further, the depths in the various bottles were in the ratio of 1, 2, 3, etc., each depth being duplicated. The bottles were then placed in a desiccator containing water and the desiccator evacuated and placed in a thermostat that could easily be regulated within one-tenth of a degree.

Evacuating the desiccator would not affect the mechanism of the water vapor movement or the ultimate equilibrium point. It would only hasten the rate at

which the water vapor moves. The samples were weighed several times the first day and once per day thereafter. As soon as the lid of the desiccator was removed, the lids were quickly placed on the weighing bottles so that none of

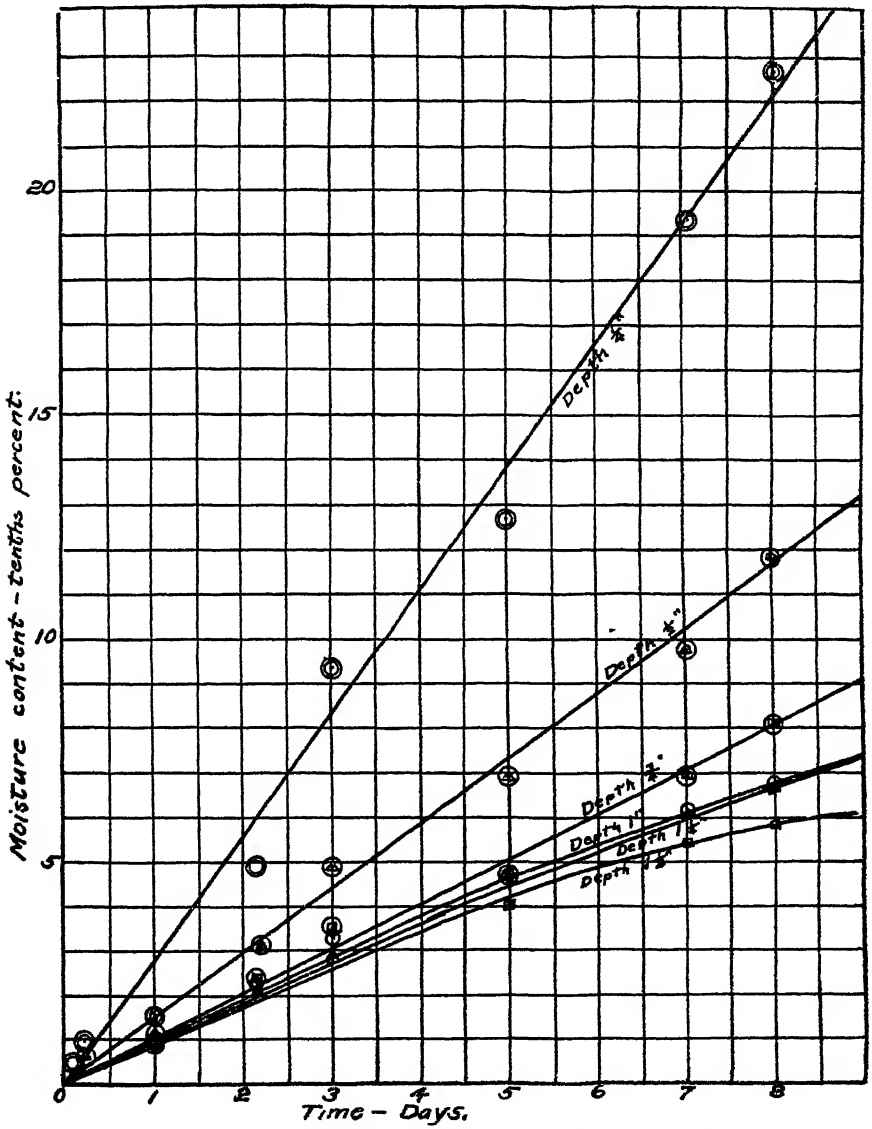

FIG. 1. RELATION BETWEEN THE MOISTURE CONTENT AND TIME

the moisture could escape. Exactly the same method of evacuating the desiccator was followed each time and the pressure inside was found to be approximately 0.7 cm. of mercury, or about one-hundreth of an atmosphere.

Quartz flour was chosen in order that all chemical and biological influences might be eliminated as far as possible.

The results obtained from weighing the bottles are shown in figure 1, the water adsorbed divided by the weight of the soil being plotted against the time. The correction for the water adsorbed on the bottles may be made in the following manner: At any given time plot the "moisture content" obtained

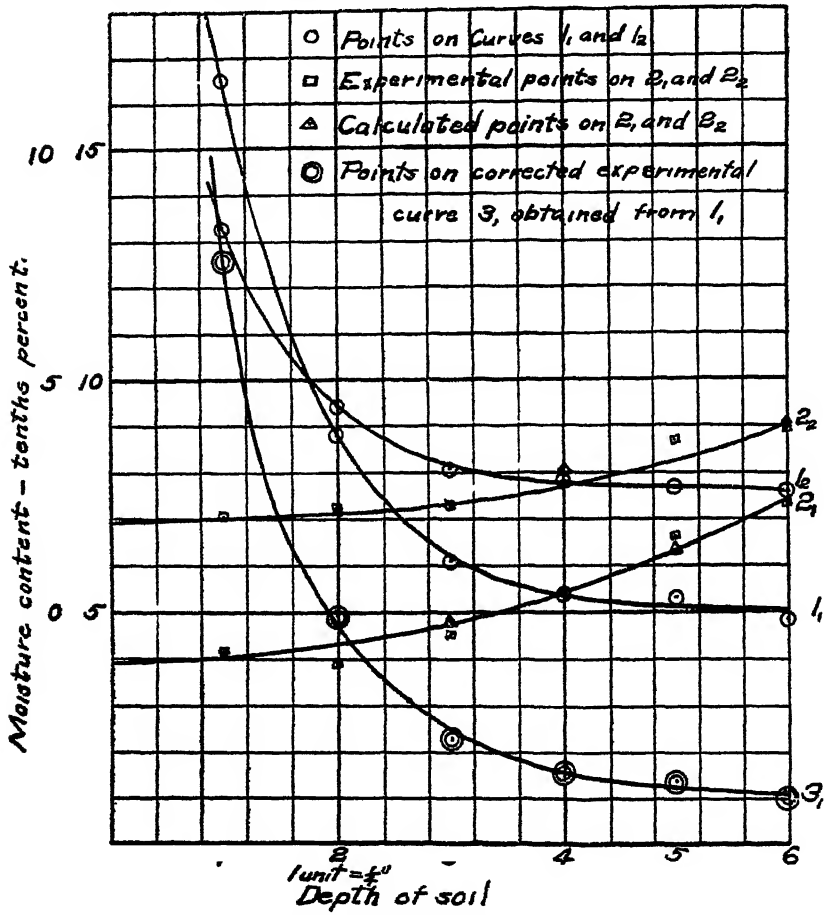

FIG. 2. RELATION BETWEEN MOISTURE CONTENT AND DEPTH OF SAMPLE

from figure 1 against the depth of soil. Taking the ordinates at time 3 and 6 the curves 1_1 and 1_2 in figure 2 are obtained. By multiplying each "moisture percentage" by the depth of the corresponding sample, curves 2_1 and 2_2 in figure 2 are obtained. The curves express the relationship between the quantity of water adsorbed and the depth of the sample at the time indicated. These same curves might be obtained directly by plotting quantity of water adsorbed against the depth at a given time from the original results. The

advantage of the method used lies in the fact that average values are obtained as compared with single values by a direct method. By extending the curves back to the Y axis, it can readily be seen that when the depth of the soil is 0 the quantity of water adsorbed is about 2 units where time is 3 and about 4 units where time is 6, which is the amount of water adsorbed on the glass. By reducing each ordinate of the curve 1_1 by this amount, the curve 3_1 is obtained which expresses the true relationship between the average moisture percentage and the depth. This curve is an hyperbola over the range indicated and its equation may readily be found. It can be seen from figure 1 that for any given depth the rate of increase of the moisture content through the range investigated is practically constant. Therefore, curves 2_1 and 2_2 in figure 2 are also curves expressing the relation between $\frac{dq}{dt}$ and the depth for a given time, which are the variables in equation (6). If the theoretical considerations upon which this equation is based are correct the equation will fit the curves 2_1 and 2_2. By using the first and last points on the experimental curves, the values of the constants A and B in equation (7) were determined and then the theoretical points on the curve calculated with these constants. The position of the calculated points can be seen in the figure. The values of the constants K_1, K_2, and K_3 cannot be determined from the experimental data. K_1 and K_3 are constants which depend only on the kind of soil used. K_2, which is the vapor density gradient, is a function of the time, and hence the values of A and B in equation (7) vary with the time, for they both contain K_2. If the value of any one of these constants is determined, the others may readily be calculated. The value of K_1 may be obtained by measuring the vapor pressure of the soil at several moisture contents as has been shown by Thomas.

This paper is an attempt to use the well-known principles of mechanics to solve the problem of water vapor movement through soils. Starting with several reasonable assumptions, an equation is developed which expresses the relation between the rate of adsorption and the depth of the soil. The results show that qualitatively the theory is in accord with the facts.

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A STUDY OF THE FERTILITY OF THE SOILS OF GREECE

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INTRODUCTION

The soils of Greece are supposed to be among the oldest in the world. They have been under cultivation for long periods of time probably measured by many thousands of years. A large majority of them have never received any commercial fertilizers or green manure and very little, if any, animal manure. The productivity of most of these soils is at present quite low—the average yield of wheat for instance, is only about 11 bushels to the acre, and this yield is produced only once every two or three years. The system of farming that most farmers follow consists of cropping the land one year and leaving it idle, or fallow, one or two years.

For these and other reasons a knowledge of the state of productivity together with the chemical composition of these soils becomes at once of deep interest and great importance. Because of their great age and neglected fertility probably few other soils in the world present so interesting and profitable a case for study and comparison as those in Greece. Many of our present ideas and theories concerning soil fertility find an excellent basis for examination and testing in the soils of Greece.

In this paper are presented some results of study of these soils. This study was conducted by the late Cyril G. Hopkins (with the writer as his assistant) who was sent to Greece by the American Red Cross and the War Board at the special request of the Greek Government to investigate the soils of that country with the main object in view of increasing their productivity. The results of this investigation formed the basis and subject matter of a report which was published and addressed to the farmers and the Government of Greece. This report has not as yet been published in English but it is the intention of the University of Illinois to do so. This report, however, was intended primarily for the Greek farmers and consequently it is presented in a popular and didactic form. Because it was intended for the Greek farmers it does not include much scientific data and many observations and facts which are of value and interest to foreign and scientific readers. It is without doubt that had Dr. Hopkins lived he would have prepared a special and more technical paper on his studies and observations of the soils of Greece, together with the fundamental lessons and conclusions they point to.

Since it was the rare good forture of the present writer to be the associate and companion of Dr. Hopkins in all of his work in Greece, he has been asked and urged by interested students of soils and soil fertility to prepare a special article embodying the essential results of the investigation on the soils of Greece. He has deemed it advisable, and has undertaken to do this with all credit and honor to Dr. Hopkins.

In the investigation of the soils of Greece four different methods were pursued: (1) personal examination, (2) chemical analyses, (3) pot-culture experiments and (4) field experiments. In this paper will be presented briefly the most essential and important findings of all four methods.

Before the experimental results are presented, however, it is considered advisable for a more intelligent and thorough understanding of them to give a brief and general description of the soils of Greece, particularly as to their topography, geology, texture, management, climate, etc. Only the most essential facts which have a bearing on the experimental results and conclusions will be considered.

TOPOGRAPHY

Greece is a very mountainous country, more than half of the area consisting of mountains. The agricultural land is situated on plateaus or broad mountain tops of mountain ranges, on gradual slopes of high mountains, on hills and ridges, on river and inter-mountain valleys, on basins, valley deltas, piedmont slopes, inter-mountain and coastal plains. The number of large plains is small and these are found mainly in Thessaly, Macedonia and Thrace. There are few in Peloponnesus but they are not so extensive in area. A large portion of the agricultural land of the country is located on hills and rock mountains. Big mountains more than a thousand feet high, very steep and rocky, are being farmed. The land on the slopes of these mountains is actually made by the farmers themselves. They make patches of land by digging out the rocks or cultivating between the rocks. In order to keep the soil from being washed away these mountains are terraced with stone walls. The farmers abandon beautiful valleys and plains and go to farm these rock mountains because their soils are newer and more productive.

On account of the mountainous and hilly nature of the country, and in view of the fact that the rainfall comes usually in torrents, much erosion and gullying takes place on the agricultural land. These erosion and gullying processes are considerably facilitated by the fine texture of the soil.

GEOLOGY

Besides being very mountainous, Greece is also a very rocky country. Solid rock, probably, composes most of the mountains and hills. On account of their steepness and deforestation many of these mountains and hills are little else than barren rocks. These rocks are mainly limestone. In a few

places they consist of schists, shales, granites, conglomerates and sandstones, but the main and predominant rock formation of the country, or outcrop, is limestone. This limestone is remarkable for its uniformly high purity. In about 50 samples collected from different parts of the country and analyzed, the relative purity ranged from about 90 to 100 per cent with most samples showing about 98 per cent calcium carbonate.

The greatest portion of the soils of Greece, therefore, have been derived from limestone rock and they are the residue of the impurities of the limestone, or of the decomposed limestone itself, as large areas of land consist mostly of decomposed limestone rock or marl.

GEOLOGICAL CLASSIFICATION OF THE SOILS

Probably all the soils of Greece will come under the following standard classification:

Sedentary
- Residual
- Cumulose

Transported
- Colluvial and alluvial
- Marine and lacustrine
- Aeolian

It will be noted from this classification that there are no glacial soils in Greece, otherwise all the above formations are represented to a more or less extent. In extent of area the alluvial soils probably rank first followed perhaps, in order, by the residual, lacustrine, marine, colluvial, cumulose and aeolian soils.

Texture of Soils

On account of the rocky nature and rough configuration of the country one would think that the agricultural land in Greece would be very stony. On the contrary, nearly all of the land in the large plains, valleys, basins, and plateaus is entirely, or almost free of stones and gravel. The agricultural land, however, on most of the mountain slopes, on many of the hills, on some of the narrow valleys, small basins and mountain tops, and on nearly all of the piedmont slopes is quite stony or gravelly. The greatest majority of the soils of Greece are of fine texture, consisting of clays,silts, and loams. There are practically no pure sandy soils in Greece. Even on most of the mountain tops, mountain slopes and hills where stones and boulders are very abundant the fine earth consists usually of clay. This fine texture of the soils may be partly indicative of their long age.

ANNUAL RAINFALL

Although Greece is a very small country, having a territory of only about 50,000 square miles (not including the new territory acquired in the Great War) its annual rainfall varies greatly between the different sections. In some of the islands and part of the mainland in the western part of old Greece the rainfall is about 46 inches while in the region around Athens it is only about 13 inches. In the greatest part of the country, however, the average annual precipitation is considerably above 20 inches.

The periodic distribution of the rainfall in almost the entire country is very unfortunate. The greatest portion of it comes in the winter months and very little, if any, in the summer months. It usually starts about October and continues until March or April with most of it falling during November, December and January. The late spring months and all of the summer months are usually very dry. In some years and in certain sections of the country there may be no rainfall at all for four or five months in succession during the warmer part of the year.

It is readily evident, therefore, that insufficient and improper distribution of rainfall must be a very serious limiting factor in the crop production of Greece.

CROPS GROWN AND THEIR YIELDS

Nearly all of the common crops are grown in Greece to a greater or less extent. Of the cereal crops wheat is the most widely cultivated followed in order of importance by corn, barley, oats, mixture of wheat and barley, rye, millet, sorghum and rice. The average yield per acre of these crops in old Greece for the year 1914 is shown in table 1.

TABLE 1

Average yield per acre of the different crops grown in old Greece in 1914

NAME OF CROP	YIELD PER ACRE
	bushels
Wheat	11.2
Wheat and barley (mixture)	11.8
Corn	18.0
Barley	16.4
Oats	19.6
Rye	11.8
Millet	12.3
Sorghum	11.0
Rice	12.0

These yields, as has already been stated, are produced mostly once every two years.

The cultivated leguminous crops grown in Greece consist almost entirely of those species that are used for human food including beans, lentils, haricots, chickpeas, peas, etc. Practically no cultivated soil improving legumes such as clover and alfalfa are grown in Greece. This is due primarily to the severely dry summers.

One of the leading and most important agricultural industries is grape, raisin, olive and citrus culture. The large areas of land devoted to these fruits were not, however, included in the investigation and consequently will not be considered in this paper.

NEGLECTED SOIL FERTILITY

One of the most neglected factors in Greek agriculture is the fertility of the soil. The farmers as a whole have done practically nothing to maintain or increase the fertility of the soil. The great majority of them have never used any commercial fertilizers on their land, and as previously stated, practically no cultivated soil-improving legumes are employed. Even the legumes which they grow for human food are usually pulled out by the roots, and so utilized that the soils derive practically no benefit from them in the way of nitrogen enrichment.

There are, however, growing on most of the agricultural land, different kinds of wild annual legumes. But on account of the frequent and close grazing by the sheep, and on account of the early and long drought, they are usually not allowed to attain any significant development. The soils during their idleness, however, probably receive some nitrogen from these wild legumes.

Farm manure is quite scarce in Greece. This is due to the fact that the chief livestock consist of sheep and goats which graze most of the time on the mountains. The only manure, therefore, that most of the agricultural land ever receives, is from the sheep and goats during grazing, and this is negligible.

CHEMICAL COMPOSITION OF THE SOILS

More than eighty samples of soils were collected from different parts of Greece representing nearly all of the most extensive and important soil types and areas of the country, and were analyzed for the total elements of nitrogen, phosphorus, potassium, magnesium and calcium, and also for limestone and acidity. For the determination of total nitrogen, phosphorus, potassium, magnesium and calcium the old "American official method" (1) was used; for the determination of the limestone and acidity, or limestone requirement, the Hopkin's Method (1, 2) was employed. The adjoining tables show the total quantities of these substances in 2,000,000 pounds of fine dry soil, and also a descriptive record of all the soils collected and analyzed. All the soils have been arranged in groups according to the regions from which they were taken.

TABLE 2

Description of soil samples

SOIL NUMBER	TOWN NEARBY	TOPOGRAPHY OF LAND	AGRICULTURAL CONDITION	CHARACTER OF SOIL	RESULTS OF ANALYSES						
					Weight of elements in an acre of 2,000,000 lbs. of air-dry soil					Limestone in an acre of 2,000,000 lbs.	Lime requirement
					Nitrogen	Phosphorus	Potassium	Magnesium*	Calcium*		
					lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	
1	Thebes	Valley slope, nearly level	Grain	Sandy clay loam	3,100	760	7,140			117,400	
2	Larissa	Hill land, rolling	Grain	Gravelly loam	2,640	650	21,560			421,400	
3	Larissa	Upland valley, nearly level	Grain	Clay	1,790	740	34,800			48,800	
4	Lamia	Valley slope, nearly level	Grain	Silt loam	2,070	1,060	25,790			76,200	
5	Lianokladi Junction	Hill land, sloping	Grain	Gravelly clay	1,870	730	13,240			160,400	
6	Arbanitsa	Piedmont, gently sloping	Grain	Clayey silt	2,610	1,680	45,300			43,000	
7	Pylos	Valley, nearly level	Grain	Calcareous clay	3,190	1,810	34,830			205,800	
8S	Gargalianoi	Plateau, nearly level	Abandoned	Subsoil clay	1,750	740	27,910	14,170	5,990		930
9	Sageika	Coastal plain, undulating	Grain	Sandy loam	1,420	1,090	16,760	3,850	6,060		60
10S	Sageika	Coastal plain, undulating	Grain	Subsoil of 9, clay	1,490	1,410	24,470	5,480	4,070		100
11S	Sageika	Coastal plain, undulating	Grain	Subsoil, clay	1,020	1,180	18,360	6,750	9,970		340

* Soils which contained much limestone were not analyzed for calcium or magnesium.

12	Lappa	Coastal plain, nearly level	Waste land, brush	Sandy clay loam	1,460	210	14,900	3,540	5,290		80
13S	Lappa	Coastal plain, nearly level	Waste land, brush	Subsoil of 11, sandy clay	1,180	530	16,730	6,600	8,490		90
14	Likochia	Mountain slope, terraced	Grain	Stony clay	5,180	2,450	43,280	18,560	22,060	23,100	
15S	Megalopolis	Ridge land, rolling	Waste land, brush	Subsoil, clay	1,780	1,250	30,910	10,290	7,860		770
16S	Imbraim	Ridge land, rolling	Waste land, weeds	Subsoil, clay	1,750	1,170	23,620	8,210	5,720		140
17	Larissa	Upland valley, nearly level	Grain	Clay (pot culture)	2,650	1,050	36,700	15,620	19,510	2,200	
18	Thebes	Valley slope, nearly level	Grain	Sandy loam (pot cultures)	3,040	1,220	10,150	46,150	42,650	86,200	
19	Sageika	Coastal plain, undulating	Grain	Sandy loam (pot cultures)	2,880	460	16,290	5,620	5,050		70
20	Sageika	Coastal plain, nearly level	Grain	Sandy loam (field experiments)	2,270	1,110	22,270	5,050	6,070		100
21	Gargalianoi	Plateau, undulating	Abandoned	Silty clay	2,870	1,020	20,880	8,920	13,900		170
22S	Gargalianoi	Plateau, undulating	Abandoned	Subsoil of 21, clay	1,770	840	24,950	15,430	12,060		6,030
23	Gargalianoi	Plateau, nearly level	Abandoned	Silty clay (culture experiments)	3,480	1,450	19,440	6,800	14,800		70
24	Kalabryta	Mountain slope, terraced	Grain	Silty clay	3,720	2,050	31,920	15,340	127,140	266,000	
25	Bysoka	Valley delta, nearly level	Grain	Gravelly sandy clay	3,960	1,410	23,180	7,430	6,210	6,300	

TABLE 2—*Continued*

SOIL NUMBER	TOWN NEARBY	TOPOGRAPHY OF LAND	AGRICULTURAL CONDITION	CHARACTER OF SOIL	RESULTS OF ANALYSES						
					Weight of elements in an acre of 2,000,000 lbs. of air-dry soil					Limestone in an acre of 2,000,000 lbs.	Lime requirement
					Nitrogen	Phosphorus	Potassium	Magnesium*	Calcium*		
					lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	
26	Megalopolis	Hill land, steep slope	Partly abandoned	Clayey silt	4,360	1,450	40,940			421,800	
27	Megalopolis	Ridge land, nearly level	Abandoned, scrub trees	Silt loam	3,410	380	16,770	5,220	5,980		70
28S	Megalopolis	Ridge land, nearly level	Abandoned, scrub trees	Subsoil of 27, clay	1,720	1,020	21,850	7,010	11,710		970
29	Megalopolis	Ridge land, undulating	Partly abandoned	Gravelly silt loam	1,990	1,320	20,370	6,160	10,690		970
30S	Megalopolis	Ridge land, undulating	Partly abandoned	Subsoil of 29, clay	1,990	1,020	27,580	8,090	2,930		50
31S	Mpilali	Ridge land, rolling	Abandoned, scrub trees	Subsoil, clay	2,320	620	38,820	20,590	7,390		13,550
32	Armeni, Crete	Valley, nearly level	Grain or fallow	Sandy silt loam	2,860	300	24,190	11,930	4,330		50
33	Armeni, Crete	Mountain slope, terraced	Grain	Calcareous clay loam	5,770	4,890	25,350			713,200	
34	Chania, Crete	Valley, gentle slope	Grain or fallow	Sandy clay loam	2,270	710	18,690	6,050	2,900		50
35S	Chania, Crete	Valley, gentle slope	Grain or fallow	Subsoil of 34, sandy clay	2,290	1,020	33,170	6,730	2,900		50
36	Souda, Crete	Mountain top, rolling	Grain	Clay	4,290	1,840	39,020	15,200	9,490	4,300	
37	Knosos, Crete	Mountain top, rolling	Grain or idle	Calcareous loam	3,130	910	13,150			1,487,400	
38	Candia, Crete	Valley, nearly level	Grain or vines	Loam	2,270	1,110	22,290			630,800	
39	Phinika, Crete	Ridge land, rolling	Grain	Calcareous loam	3,430	1,430	25,470			860,400	

40	Korytsa	Low valley, nearly level	Grain or meadow	Clayey silty loam	4,250	1,670	42,320			88,400	
41	Korytsa	Valley delta, steep slope	Grain or fallow	Sandy clay loam	2,310	1,240	19,000	7,360	43,520	1,900	
42	Korytsa	Hills or valley ridges	Grain or fallow	Clayey silt loam	2,320	1,450	47,200	12,400	22,460	11,800	
43	Yannina	Mountain top, rolling	Grain or fallow	Cherty clay	4,400	11,720	22,350			42,800	100
44	Soudovitra	Valley, gentle slope	Grain or fallow	Silty clay loam	2,900	3,520	32,200	10,980	16,000		100
45	Yannina	Ridge land, undulating	Pasture	Silt loam	2,320	1,830	22,060	6,450	9,440		530
46S	Yannina	Ridge land, undulating	Pasture	Subsoil of 45, clay	2,010	1,430	26,850	11,430	6,150		2,440
47	Keletron	Ridge land, undulating	Grain or fallow	Clayey sandy loam	2,280	1,010	30,660	1,760	4,180		50
48S	Keletron	Ridge land, undulating	Grain or fallow	Subsoil of 47, sandy clay	2,230	1,210	36,690	4,430	3,330		70
49	Keletron	Valley land, nearly level	Grain	Clay, very gummy	2,860	610	23,790	9,470	8,020		100
50S	Keletron	Valley land, nearly level	Grain	Subsoil of 49, clay	1,760	1,050	38,380	17,770	15,750		1,120
51	Kastoria	Mountain slope, terraced	Grain and vines	Clay loam	2,590	1,640	45,490			91,600	
52	Pella	Ridge land, undulating	Grain or idle	Clay loam	2,930	1,680	47,490			126,400	
53	Koutsopodi	Hill land, rolling	Grain or fallow	Calcareous silt loam	2,570	1,020	17,160			1,158,800	
54	Argos	Steep piedmont slope	Grain	Very strong clay loam	4,390	1,670	39,900			38,800	
55	Argos	Valley gentle slope	Grain	Stony sandy loam	2,280	1,530	26,680			97,400	

TABLE 2—*Concluded*

SOIL NUMBER	TOWN NEARBY	TOPOGRAPHY OF LAND	AGRICULTURAL CONDITION	CHARACTER OF SOIL	RESULTS OF ANALYSES						
					Weight of elements in an acre of 2,000,000 lbs. of air-dry soil					Limestone in an acre of 2,000,000 lbs.	Lime requirement
					Nitrogen	Phosphorus	Potassium	Magnesium*	Calcium*		
					lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	
56	Tatarí	Hills or ridges, rolling	Grain or fallow	Silty clay loam	3,800	1,040	27,030			411,000	
57	Magoula	Valley, nearly level	Grain or fallow	Clay loam	3,000	750	35,410	17,510	26,830	4,800	
58	Pharsala	Valley, nearly level	Grain	Silty clay loam	4,160	2,550	26,810	45,230	43,710	12,600	
59	Lazarina	Plain, nearly level	Cotton	Silty clay loam	3,180	1,860	37,380	28,340	18,120	6,800	
60	Kapudji	Valley, nearly level	Grain or forage	Sandy silt loam	2,880	1,550	21,010	45,590	63,020	5,200	
61	Salonica	Hill land, rolling	Grain or fallow	Clayey silt loam	2,890	1,030	19,710			274,800	
62	Dobitsa	Mountain slope, terraced	Grain or fallow	Silty clay, stony	2,870	1,020	32,840			730,400	
63	Dobitsa	Hill land, rolling	Grain or fallow	Gravelly clayey loam	2,320	1,040	42,630			509,000	
64	Zichna	Ridge land, undulating	Grain or pasture	Clayey silt loam	2,040	1,660	57,210			85,200	
65	Serres	Valley, gentle slope	Grain or pasture	Sandy loam	1,700	2,020	64,490			88,200	
66	Drama	Piedmont slope, gentle	Grain or fallow	Clay loam	3,030	1,520	38,990	15,290	27,450	10,400	
67	Dokzat	Ridge land, undulating	Grain or fallow	Clayey sandy loam	1,840	810	30,440	3,100	5,060		70
68S	Dokzat	Ridge land, undulating	Grain or fallow	Subsoil of 67, clay	1,460	730	33,390	4,290	3,720		50
69	Philippi	Plain, nearly level	Abandoned	Sandy silt loam	1,990	410	38,430	3,420	10,300		50
70	Drama	Plain, nearly level	Abandoned	Clay	2,650	730	23,490	5,250	12,330		70

71	Boutianoi	Mountain slope	Grain or fallow	Shaly loam	2,280	1,220	45,050	15,560	6,530		70
72	Sparta	Hills and ridges	Grain or fallow	Calcareous loam	2,850	1,530	21,730			563,000	
73	Kamary	Mountain slope, terraced	Grain or fallow	Silty clay	4,100	1,880	39,930	15,140	23,610	9,400	
74	Tripolis	Hill land, rolling	Grain or fallow	Stony loam	2,570	1,430	32,750			81,800	
75	Tripolis	Valley, nearly level	Grain or forage	Silt loam	2,570	1,120	23,480	31,390	14,600		50
76	Liopesi	Piedmont slope	Grain or fallow	Very stony loam	3,160	2,050	32,220			201,600	
77	Marathon	Piedmont slope	Grain or idle land	Stony loam	4,020	1,540	36,850	17,550	28,580	5,200	
78	Marathon	Piedmont slope	Grain or fallow	Sandy loam	2,280	1,630	25,000			181,800	
79*	Marathon	Coastal plain, level	Rice or corn	Calcareous muck	6,540	670	2,520			719,500	
80S	Marathon	Coastal plain, level	Rice or corn	Subsoil of 79, calcareous clay	3,480	930	40,210			607,400	
81	Sageika	Coastal plain, level	Grain or pasture	Clay over marl	2,050	520	22,330	12,580	20,320	6,000	

* No. 79 is a muck soil and the weights reported are found in 1,000,000 pounds per acre, representing about 6¾ inches in depth.

The foregoing analytical data reveal many interesting and important facts. First of all they show that the soils of Greece differ very greatly in fertility as measured by chemical analysis. Thus nitrogen, in the plowed soil, varies from 1420 pounds per acre in soil no. 9 to 5770 pounds in soil no. 33. Out of 81 soils examined, 65 are surface soils. The nitrogen variation in these surface soils is shown in table 3.

Of the three soils which contain more than 5000 pounds of nitrogen, two came from among limestone rocks and terraces on the mountain slopes, and one from muck land; while of the eight soils which contain less than 2000 pounds, three came from level plains, two from valleys, one from hill land, and two from ridge land. Of the eight soils which contain an amount ranging between 4000 and 4500, two are located on piedmont slopes, two on mountain tops, one on a mountain slope, one on hill land, one in a valley, and one in a low valley. It seems evident, therefore, that most of the soils richest in nitrogen are found on mountain and piedmont slopes, while the soils poorest in nitrogen are generally located in level plains and in some of the large valleys.

TABLE 3

Nitrogen in surface soils

NITROGEN CONTENT	NUMBER OF SOILS WITHIN GROUP
lbs. per acre	
1500–2000	8
2000–2500	14
2500–3000	19
3000–3500	10
3500–4000	3
4000–4500	8
5000–6500	3

There are only 14 soils out of the 65 which contain more than 3500 pounds of nitrogen and 41 contain less than 3000 pounds. It appears, therefore, that most of the soils of Greece are either poor or very poor in nitrogen. Considering, however, that most of these soils have probably been farmed for many hundreds, if not thousands, of years, without any attempt to maintain or increase their nitrogen content, it is significant that they contain as much of this element as they do.

Only 8 out of 65 surface soils and none of the subsoils contain more than 2000 pounds of phosphorus. All of these soils are on mountain slopes or low mountain tops or near the foot of mountains. Three of these soils, no. 44, 58 and 65, are composed of material washed down from nearby mountains. The other quite similar mountain soils contain 1840 pounds in no. 36, 1640 pounds in no. 51, and 1880 pounds in no. 73. Other soils from piedmont slopes which seem comparable are no. 6,54,66 and 77; also no. 7 represents a deposit washed from nearby mountain regions. These soils contain between 1500 and 2000 pounds of phosphorus. Soils no. 26, 37 and 62, although hill and

mountain slopes, average nearly half limestone, which seems to account for their low phosphorus contents.

In general, soils which have been formed from recent decomposition of limestone, and do not still contain large amounts of limestone in the fine earth, are either rich in phosphorus or moderately well supplied. These are found among the limestone rocks on the mountains, on some piedmont slopes and in some valley deposits washed from such mountain regions. The more common soils of Greece, however, vary from poor to very poor in phosphorus. This is true of the great coastal and inland plains of the broad intermountain valleys and plateaus, and of the low hills and ridges. Most of the agriculturally abandoned lands are very poor in phosphorus. Of the five soils which contain less than 500 pounds of phosphorus three are situated on level plains, one in a valley and one on a level ridge land. Of the twelve soils whose phosphorus content varies from 500 to 1000 pounds five are located in valleys, three in plains, two on hill lands, one on a mountain top and one on ridge land.

TABLE 4

Phosphorus in surface soils

PHOSPHORUS CONTENT	NUMBER OF SOILS WITHIN GROUP
lbs. per acre	
200– 500	5
500–1000	12
1000–1500	23
1500–2000	17
2000–2500	4
2550	1
3520	1
4890	1
11,720	1

Potassium, though quite abundant, varies from 2500 pounds in soil 79 (muck) and 7,140 pounds in soil 1 to 64,490 pounds in no. 65. On the whole, all of the normal soils examined are well supplied with potassium and most of them are very rich in this element.

Magnesium ranges from 1760 pounds in soil no. 47 to 46,150 pounds in no. 18. Many of the soils contain a large amount of magnesium.

Calcium varies from only 2900 pounds in soil no. 34 to 127,140 pounds in no. 24. Soils which contained much limestone were not analyzed for calcium or magnesium. Such soils, of course, would indicate a greater amount of calcium than is shown in the maximum figure above.

Limestone ranges from none at all in several soils to 1,487,400 pounds in soil no. 37. Most of the soils of Greece are abundantly supplied with limestone.

The limestone requirement varies from none in most soils to 13,550 pounds in soil no. 31. The acid soils form a fairly large aggregate area and are scat-

tered in many widely separate regions. They are usually found on plains, ridges, hills, or plateaus, which have lost their original supply of limestone and which can not receive additional supplies washed down from higher lying lands. Of such soils included in this study, 15, 16 and 27–31 are situated on ridge lands near the center of a great valley; no. 8, 21, 22 and 23 are found on a plateau; no. 34 and 35 are situated on a sloping land in the center of a valley or coastal plain; no. 45 and 46 are found on low broad ridges in the center of a valley; no. 47 and 50 are located on ridge land and coastal plain across a lake; and no. 67–70 are found in a great plain.

Many soils were found abundantly supplied with limestone at a depth of 3 feet and more which, however, were very acid at the surface. Some of these subsoils testd as much as 50 per cent of calcium carbonate.

POT CULTURE TESTS

Although the time that the commission remained in Greece was only about a year, it managed to conduct a few pot culture and field tests. The object of these tests was to secure additional information and to verify, if possible, some of the analytical data. In the pot culture experiments, sweet clover was grown in 38 earthenware jars having a diameter of about 8 inches and a depth of about 10 inches. The following treatments, and combinations thereof, were used:

	gm.
Acid phosphate	6.000
Sodium chloride	2.975
Potassium chloride	3.730
Ground limestone (where needed)	150.000

The soils employed were no. 17, 18, 19 and 23. Each test was run in duplicate series, A and B. The sweet clover plants were allowed to grow for about three months when the tops were cut and weighed immediately (see tables 5 and 6).

An examination of these results shows that phosphorus produced a marked increase in yield in every case. Soils no. 18 and 17 both contained limestone, but where applied to acid soils no. 19 and 23, limestone gave a large increase in every case, whether applied alone or in addition to phosphorus and potassium.

After harvesting the sweet clover it was partially dried and mixed together with the roots into the soil, and millet planted. The nitrogen contained in the sweet clover turned under resulted in large growth by the millet over the check.

FIELD TESTS

Temporary field tests, eight in number, were inaugurated in different parts of Greece on soils representing typical and large areas. The underlying principle of all these experiments was to show the effect of phosphorus and

TABLE 5

Relative effects of phosphorus, sodium and potassium on soil not in need of lime

POT NUMBER	TREATMENT	WEIGHT OF GREEN TOPS OF CLOVER PLANTS				AVERAGE
		Soil number 17 from Larissa		Soil number 18 from Thebes		
		Series A	Series B	Series A	Series B	
		gm.	*gm.*	*gm.*	*gm.*	*gm.*
2	Nothing	38	41	30	18	32
3	Acid phosphate	95	108	104	112	105
4	Acid phosphate–NaCl	84	84	125	132	106
5	Acid phosphate–KCl	82	74	116	118	97

TABLE 6

Relative effect of phosphorus, sodium and potassium on soil in need of lime

POT NUMBER	TREATMENT	WEIGHT OF GREEN TOPS OF CLOVER PLANTS				AVERAGES	
		Soil number 19 from Sageika		Soil number 23 from Gargalianoi		Four pots	Eight pots
		Series A	Series B	Series A	Series B		
		gm	*gm*	*gm*	*gm.*	*gm.*	*gm.*
2	Nothing	19	25	10	4	14	
3	Ground limestone	63	39	23	22	37	34
4	Ground limestone, acid phosphate	76	67	71	62	69	87
5	Ground limestone, acid phosphate, NaCl	84	89	74	82	82	94
6	Acid phosphate, NaCl, KCl	85	90	72	80	82	90
7	Acid phosphate, KCl			30	28	29	

TABLE 7

Effect of acid phosphate and lime on growth of sweet clover

SOIL TREATMENT	YIELD PER ACRE OF DRY HAY	
	Soil 19, Sageika	Soil 23, Gargalianoi
	lbs.	*lbs.*
None, check	150	220
Limestone	740	850
Limestone, acid phosphate	3090	3150
Acid phosphate	310*	510

* Computed from later harvest.

lime on the growth of sweet clover, and in turn the beneficial influence of this when incroporated with the soil on the grain crops. In this paper the results of only two representative experiments will be presented. One of these experiments was conducted on soil 19 and the other on soil 23, both of which were also employed in the pot culture tests. Phosphorus was applied at the rate of about 800 pounds of acid phosphate, and limestone at the rate of about ten tons to the acre. The clover seed was planted on the field represented by soil 19 on January 10 and the crop was harvested on June 28, of the same year. On the field represented by soil 23 the seed was planted on January 15 and the crop was harvested on June 26. It must be remembered that both of these soils are acid. The yield of dry clover hay produced by the different treatments at each field is shown in table 7.

It will be readily seen that at both fields all the treatments caused a very marked increase in the yield of sweet clover. The greatest increase, however, occurred where both limestone and phosphate were applied.

In our travels through Greece it was observed that the soils of the country are very susceptible to fertilization, especially with phosphorus and nitrogen, and that acid soils are much improved by treatment with limestone.

SUMMARY

It is a matter of record that the average yield of grain crops in Greece is low and that the average yield of wheat is only about 11 bushels to the acre. These low yields are generally produced only once in two years because of the common practice of fallowing.

Three main factors are responsible for this low yield of grain crops. These are (1) poor and unclean seed and weedy stand of plants, (2) insufficient rainfall in the late spring and in the summer and (3) low content of the nitrogen and phosphorus in most of the common soils and the almost complete failure of the farmers to supply these elements to the soil in the form of fertilizers or manures.

There is no question that both of the first two factors, and especially the second, play a considerable rôle in limiting the yield of grain crops on the soils of Greece. But the chief limiting factor has been the loss of soil fertility. Where nitrogen and phosphorus are present in sufficient amounts, the soils were reported to produce fairly good crops even in dry seasons. On soils very low in these elements the crops were almost a failure in the dry season.

The chemical analysis of over 80 representative types of soils shows that the soils of Greece vary very greatly in fertility. Thus nitrogen, in an acre of 2,000,000 pounds of surface soil varies from 1500 to 5000 pounds; phosphorus from 210 to 11,720 pounds; potassium from 2520 to 64,490 pounds; magnesium from 1760 to 46,150 pounds; calcium from 2900 to 127,140 pounds; limestone from 0 to 1,487,400 pounds; and acidity from 0 to 12,550 pounds limestone equivalent.

With the exception of a few abnormal soils, all of the soils examined are well supplied with potassium.

Limestone is present in abundance in most of the soils of Greece. There are some soils, however, scattered in many widely separate regions, that contain no limestone and are acid. These are usually found on level plains, ridges, hills and plateaus, which have lost their original supply of limestone and which can not receive additional supplies washed down from high lying land. On the whole, however, acid soils in Greece are comparatively few.

It was found that many beautiful plains with soils of good physical conditions were agriculturally abandoned, because the new soils of the mountain slopes produce more profitable yields.

Chemical examination shows that the soils of these mountain slopes are usually richer both in nitrogen and phosphorus and especially in the latter, than those of the plains. The soils richest in nitrogen and phosphorus and usually the most productive, were found on the terraces of the mountain slopes, on the sides and bottoms of small valleys between hills, ridges or mountains and on the bottom of big valleys overflowed with river water. The poorest soils in nitrogen and phosphorus and usually the least productive, were found on level plateaus, tops of hills and ridges, and on some of the level plains which neither receive deposits by overflow nor lose partially depleted soil by erosion.

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THE NATURE OF CERTAIN ALUMINUM SALTS IN THE SOIL AND THEIR INFLUENCE ON AMMONIFICATION AND NITRIFICATION

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INTRODUCTION

That soluble salts of aluminum are present in acid soils in considerable quantities, and that these salts may be largely responsible for soil acidity, are conclusions that have been reached by several investigators. The literature on aluminum in its relation to soil acidity has been fully reviewed by Mirasol (10). No attempt, therefore, will be made in this paper to treat the subject historically, especially in view of the fact that the problem to be discussed deals in part with the influence of aluminum salts on bacterial activity, on which subject little work has been reported. References to the literature will be made from time to time as they bear directly upon the particular topic under discussion.

The toxicity of soluble aluminum salts toward farm crops has been clearly demonstrated by Hartwell and Pember (5), Abbott, Conner and Smalley (1), Mirasol (10), and by the writer in some preliminary work, which in view of its agreement with what has been reported, need not be considered further. There does not appear, however, to be such definite information regarding the effect of these salts upon the important bacterial processes of ammonification and nitrification. In view of the fact that the hydrolysis of the sulfate, chloride and nitrate of aluminum produces a strongly acid medium, it would be expected that the nitrifying organisms would be affected adversely by the presence of these salts in the soil. Furthermore, since it has been maintained by some investigators, and particularly by Mirasol, that the origin of soluble aluminum salts in the soil is for the most part to be ascribed to bacterial activity, it became desirable in planning this work to study this factor also.

[1] The successful termination of the work herein reported is due in no small measure to Dr. Albert L. Whiting, under whose supervision the investigation was carried out. It is the intention of Doctor Whiting to continue investigations on the problem of aluminum in its relation to soil bacteria and acidity, the results of which should contribute to a more complete understanding of the whole question of soil acidity.

THE NATURE OF CERTAIN ALUMINUM COMPOUNDS IN THE SOIL

Before attempting experimental work involving a study of bacterial activity as influenced by aluminum salts, it was deemed essential to investigate in some detail the exact nature of the aluminum compounds of the soil which might be involved in the problem under consideration. Merely to group all the aluminum compounds that might be extracted from the soil under a single head, namely, as being toxic to plant growth, seemed to be wholly unwarranted because of the widely differing nature of the aluminum compounds concerned. For this reason, it has been considered well to review very briefly the opinions that are held with respect to the character and origin of these compounds before entering into a discussion of the experimental work to be reported.

Theories on the formation of soluble aluminum in soils

Probably one of the first investigators to give attention to the presence of aluminum in the soil from the standpoint of soil acidity was Veitch (15). In his study of the Hopkins' method for the determination of soil acidity, he attributed the acidity of the soil extract to hydrolyzed aluminum salts which had been formed by the basic ion of the neutral salt solution used as an extractant in the determination, replacing the aluminum in alumino-silicates. Truog (14) holds much the same view, stating that the treatment of an acid mineral soil with a salt solution results in the exchange of an equivalent amount of iron and aluminum for the base taken up. The iron and aluminum go into solution as salts and since they are strongly hydrolyzed in solution, they enter into the titration much the same as an equivalent amount of acid. The conception that the presence of these salts is to be ascribed to true displacement by the basic ion of the salt solution receives further support, according to Truog, from the fact that acetates bring aluminum and iron into solution as well as salts of the stronger mineral acids. It is improbable, in his opinion, that the dilute acetic acid formed by removal of the base would dissolve iron and aluminum compounds to saturation.

A second theory to explain the presence of aluminum in neutral salt extracts of soil is that held by Parker (11), who assumes that aluminum is brought into solution by a side reaction of free acid formed by the removal of the basic ion of the salt solution by selective adsorption. Knight (9) takes much the same view, asserting, however, that the basic ion is removed to make up the deficiency of bases in the acid soil rather than by the physical adsorption. The mineral acid thus formed from the acid ion of the salt solution then attacks insoluble aluminum and brings it into solution as the salt of the mineral acid as is assumed by the replacement of bases theory. This is a very important point. It is the starting point of much of the work that will be reported later.

In addition to the two theories that have been mentioned to account for the rise of soluble aluminum compounds in the soil, attention should be

directed to a third, namely, the biochemical origin of soluble aluminum. Abbott, Conner, and Smalley (1) reported, in 1913, the presence of aluminum nitrate in a peat soil and attributed its rise to nitrification taking place in the absence of a more suitable base than aluminum. This idea has been developed recently by Mirasol. From the work by Ames and Boltz (2) it would appear that aluminum may be brought into solution also as the sulfate in the process of sulfofication.

There have been presented, then, three explanations of the existence of soluble aluminum in the soil: first, that it is brought into solution by replacement of bases from alumino-silicates; second, that it is produced by the action of acid formed by withdrawal of the base from a neutral salt solution; third that is has its origin in the normal processes of nitrification and sulfofication.

An understanding of which of these three processes actually occurs or whether they all take place in the soil, while of considerable value, is of secondary importance to a knowledge of the actual chemical compound into which aluminum enters and as which it exists in the soil solution. To illustrate, if aluminum salts of the mineral acids are constantly being produced in some acid soils, the theory that has now been fully accepted by many, that active aluminum is an important factor in acidity would appear to receive added confirmation. If, however, the soluble aluminum of the soil is present as the hydroxide, as the work of Knight indicates, and not as salts, then aluminum ceases to be the important factor that it is claimed to be and becomes no more than a measure of acidity, the actual cause of which lies much deeper, but which is as yet not understood.

The presence of soluble aluminum hydroxide in soil extracts

A review of the work of Knight may serve to bring out more clearly the point just mentioned. In his study of the Hopkins' method for soil acidity, Knight found that the aluminum present in the potassium nitrate extract of an acid soil was only slightly less than enough to account for the total acidity of the extract as measured by titration with standard alkali. Basing his reasoning on the work of Blum (3), who showed that aluminum hydroxide is completely precipitated before the hydrogen-ion concentration of the solution reaches pH=7, and, conversely, that it must pass into solution when the hydrogen-ion concentration rises above this value, Knight inferred that the aluminum which he determined in the extract was present as the hydroxide. The extract was then subjected to dialysis with the result that none of the aluminum contained within it diffused through the membrane; whereas three-fourths of the total acidity of the extract was found to have diffused. On neutralization of the contents of the collodion flasks, aluminum hydroxide was precipitated. The logical interpretation of the result of this experiment is that the aluminum extracted from the soil by a neutral salt solution is present not as the easily diffusible salt, the nitrate in this case, but as soluble aluminum hydroxide.

Additional support of this contention is provided by the investigations of Rose (12), from which it appears that precipitated aluminum hydroxide passes readily into the hydrosol condition in the presence of very weak acid, namely 4 per cent acetic acid and N/20 to N/35 hydrochloric or nitric acid. He explains this formation of hydrosols as being due to the forming of a series of hydrated oxides, those hydrates containing the largest number of molecules being produced first. In studying the solubility of aluminum hydroxide in acetic acid, Rose found that hydrates having the formulas $Al_2O_3 \cdot 7H_2O$ and $Al_2O_3 \cdot 6H_2O$ were produced first, swelling up and setting as gelatinous masses. With the addition of more acetic acid $Al_2O_3 \cdot 4H_2O$ to $Al_2O_3 \cdot 2.75\ H_2O$ formed, giving only weakly opalescent solutions. As soon as the degree of hydration passed below the last value with additional acid, a hydrosol no longer formed and normal aluminum acetate resulted.

It would seem, then, that this action of weak acids on aluminum hydroxide might easily explain the presence of soluble aluminum in the soil. The weak acid of the soil or the acid produced by the withdrawal of the basic ion from a salt solution reacts with colloidal aluminum hydroxide and produces a solution that is, to all intents and purposes, perfectly clear, but which contains aluminum in a form which will not pass through a semi-permeable membrane. That there are considerable quantities of aluminum hydroxide in soils is the conclusion reached by Mirasol so that there seems to be no reason why the conversion of aluminum hydrogels to hydrosols should not take place within the soil. It should be mentioned in this regard that, according to the work of Rose, the aluminum hydroxide need not be in the gelatinous condition, i.e., as when precipitated by ammonium hydroxide, in order to enter the sol state. Perfectly dry aluminum hydroxide will pass readily into the sol provided it has not been dried at too high a temperature. The application of this principle to soil conditions is, of course, that the hydroxide in the soil need not be in the plastic condition associated with wet clay in order to form the sol but it may be simply a finely divided powder. In summary, if this principle of the reversibility of aluminum hydrogels to hydrosols obtains within the soil, aluminum passes into the soil solution not as the diffusible salt of an acid but as the indiffusible hydroxide. Not only does this theory appear plausible but it offers a ready explanation for the fact that Knight was unable to bring about diffusion of aluminum from a collodion flask. The tendency, however, of increasing soil acidity would be eventually to convert aluminum hydroxide to soluble salts of aluminum.

Data from a totally different source tend toward substantiation of the theory that has just been proposed. Reference is made to the extremely large quantities of aluminum which Mirasol succeeded in leaching from three acid soils by extracting with potassium nitrate and water until the last portions of the percolate showed in each case no titratable acidity. After drying, the soils were analyzed for aluminum, the difference in the aluminum content of the leached and unleached soil being taken as the active aluminum normally to be

found in the soils. Table 1 has been compiled from the results of analysis as reported by Mirasol.

Now it is obvious that the enormous quantities of aluminum represented in the table as having been extracted from the soils could not have been completely combined with nitrate, chloride, sulfate and phosphate ions, as the total of these acid ions could account for but a small fraction of the aluminum. It is conceivable that extraction of the soils with potassium nitrate may have converted aluminum combined as aluminum silicates into aluminum nitrate, through replacement of aluminum by potassium, but no such explanation is offered to explain the high quantities of aluminum in the water extract.

TABLE 1

Pounds per acre of aluminum in soil, determined from potassium nitrate and water extracts (2,000,000 pounds to depth of 6⅔ inches)

SOIL	TOTAL ALUMINUM IN ORIGINAL SOIL	ALUMINUM IN POTASSIUM NITRATE EXTRACT	ALUMINUM IN WATER EXTRACTS
	lbs.	*lbs.*	*lbs.*
Gray silt loam	121,000	54,200	21,400
Yellow-gray silt loam	151,200	90,600	33,400
Yellow silt loam	149,400	75,600	32,200

TABLE 2

Soluble alumina in water extracts of soils as reported by Kelley (extraction of air-dry soil)

SOIL NUMBER	ALUMINA	SOIL NUMBER	ALUMINA
	p. p. m.		*p. p. m.*
74	11 1	416	17.6
164	7.5	417	15.3
9	4.8	406	10.3
292	16.6	428	4.4
290	19.1	426	2.9
405	7.6	448	4.9

Finally, in regard to the quantity of soluble aluminum in soils, it is necessary to state that no analyses of water extracts of soils for aluminum that have come to the attention of the writer have revealed more than insignificant quantities of aluminum. Typical of such analyses are the data reported in table 2, which have been reproduced from the work of Kelley (8). These soils, according to Kelley, are acid in reaction although they contain bases. Calculated on the basis of elemental aluminum the results would be one-half of the figures given.

Having established the nature of the compounds in which the soluble aluminum of the soil exists, it would be desirable to throw further light on the conditions surrounding the rise of these compounds in the soil, particularly of the nitrate and sulfate. Several investigators have reported the formation of the

nitrate and sulfate in the soil, namely Abbott, Conner and Smalley (1) Ames and Boltz (2), and Ruprecht and Morse (13). Although it seems probable that these salts exist in very acid soils in quantities sufficient to exert a toxic effect, some doubt exists as to whether the salts were actually present in the quantities reported. At any rate, the soluble hydroxide could have been produced under the conditions of the experiments, and it would have to be eliminated as a factor before the soluble aluminum which is produced in nitrification, sulfofication and by the application of ammonium sulfate could be said to be combined with the particular acid concerned. In other words, the increased acidity that is produced in these processes could readily convert aluminum hydroxide to the hydrosol, but as soon as the acidity of the soil reaches a sufficiently high point, aluminum nitrate and sulfate are certain to be produced.

EXPERIMENTAL

The nature of the problem

It is evident from the foregoing discussion that considerable doubt exists as to the exact form in which soluble aluminum occurs in the soil; whether it occurs principally as salts of the soil acids or whether it is to be found in greater quantity in the form of soluble hydroxide. Until definite information which pointed in one way or the other was obtained, little progress in bacteriological studies could be made. If aluminum salts do not occur in soils in appreciable quantities, then their influence on bacterial activity, while of considerable scientific interest, is hardly of practical value from the standpoint of soil fertility. Consequently, before attempting bacteriological work definite information as to the form in which aluminum salts occur in the soil was sought.

A means of differentiating quantitatively between aluminum as salts and aluminum as the hydroxide was needed. Dialysis at once suggested itself as the most logical means of effecting this result. In respect to the completeness of separation of diffusible aluminum salts from the hydroxide by dialysis, there can be no question, for Jones (6), reviewing the work of Graham on dialysis of aluminum chloride from aluminum hydroxide, states that the aluminum chloride dialyzed without undergoing decomposition and that no trace of chloride was to be found in the alumina after the process had been completed. This statement also removes any doubt as to whether the aluminum salts in passage through the membrane are dissociated into the acid ion and aluminum hydroxide. Furthermore, it is a principle of dialysis that the membrane itself has no influence on the rate of diffusion of molecules sufficiently small to pass through the membrane. Therefore, since aluminum salts diffuse rapidly like any other electrolyte no difficulty should be experienced in effecting complete separation of the salts from the hydroxide. Determination of aluminum after dialysis in the diffused portion and in that portion remaining within the membrane gives at once the quantity of both forms of aluminum in the extract. A method of differentiating the forms of aluminum having been

found, this phase of the problem was reduced to the matter of preparing neutral salt extracts of several acid soils and subjecting them to dialysis.

If aluminum salts are to be found in acid soils, then a complete extracting of the water-soluble acidity of these soils must reveal the presence of aluminum in the extract, since the nitrate, chloride and sulfate of aluminum are easily extractable by water.

Experimental work carried out along the lines that have been suggested should determine the quantity of aluminum as salts of the mineral acids, likely to be found in acid soils. It would then be necessary to ascertain whether the rise of soluble aluminum in the soil is to be ascribed to the replacement of aluminum by other bases or whether it has a biochemical origin or whether both processes may account for its presence. The incubation of aluminum in solution cultures of nitrifying organisms containing no free base but aluminum, and subsequent determination of nitrate and aluminum in the cultures would indicate whether aluminum is rendered soluble in nitrification, or in other words, whether it may serve as the base in nitrification. Likewise incubation of soil with sulfur and dialysis of the extract should show whether soluble aluminum may be formed in sulfofication.

Having determined the quantity of soluble aluminum salts in acid soils, an experiment would be carried out to ascertain whether ammonification and nitrification might be inhibited in such concentrations of salts. Incubation of soil with several concentrations of the aluminun salts likely to be found in the soil should answer this question.

If inhibition of nitrate production should result from the toxicity of aluminum it would be desirable to know what fertilizer material or soil amendment would be most effective in rendering the aluminum inactive.

Description of the soils used

The soils studied in this investigation were the same as those used by Mirasol in his work to which several references have been made. The chemical analyses of these soils as reported by Mirasol are reproduced herewith; quantities are expressed as pounds per acre, assuming that the surface soil to a depth of 6⅔ inches weighs 2,000,000 pounds, table 3. In addition, a slightly acid brown silt loam from the University South Farm and soil from plot 23 of the Rhode Island Agricultural Experiment Station were used for special studies. The soil of plot 23 has received applications of ammonium sulfate since 1893 and it is extremely acid.

Experiment 1. The nature of the aluminum compounds extracted with potassium nitrate

Using for this experiment the gray, yellow-gray, and yellow silt loams and the Rhode Island soil, an extract of each was made by adding to 100 gm. of soil in a 400 cc. bottle, 250 cc. of a normal potassium nitrate solution, shaking

for 3 hours, and after the supernatant liquid had become perfectly clear, drawing off 125 cc. of the solution for analysis of aluminum. Aluminum was determined in the usual way, by precipitation with ammonium hydroxide. The precipitates were but faintly tinged with the brownish color of ferric hydroxide so that no attempt was made to separate iron from aluminum. As a check upon the results obtained by this procedure, the phenyl hydrazine method for the determination of aluminum was carried out as given by Hillebrand (6). Practically identical results were obtained. Table 4 gives the results of these determinations as the average of triplicate analyses.

TABLE 3

Chemical composition of soils used

CONSTITUENTS	GRAY SILT LOAM	YELLOW-GRAY SILT LOAM	YELLOW SILT LOAM
	lbs. per acre	*lbs. per acre*	*lbs. per acre*
Nitrate nitrogen	26	36	60
Total nitrogen	2,900	1,370	1,966
Phosphorus	1,104	693	691
Potassium	25,130	35,800	29,000
Calcium	4,510	3,920	7,850
Magnesium	4,520	4,180	5,330
Iron	47,800	74,200	74,200
Manganese	840	786	660
Aluminum	121,000	151,000	149,000
Lime requirement	2,125	2,814	2,921

TABLE 4

Aluminum in potassium nitrate extract, after 3 hours' shaking

SOIL	ALUMINUM
	lbs. per acre
Gray silt loam	678
Yellow-gray silt loam	540
Yellow silt loam	366
Rhode Island soil, plot 23	498

These figures, of course, do not represent the total soluble aluminum of the soil since no more can be extracted after equilibrium has been established between the extractant and the soil. Fresh potassium nitrate and renewed shaking would of course bring more aluminum into solution. Aliquots of a second similar series of extracts were than pipetted into 500-cc. collodion flasks for dialysis. These flasks were suspended in separate glass jars containing 3 liters of distilled water and dialysis allowed to take place for 2 days. During each day, water was constantly drawn off and evaporated. Finally, when 1 liter of the diffusate after evaporation to several cubic centimeters

gave no test for nitrate with diphenylamine sulfuric acid, it was assumed that the process of dialysis was complete. The diffusate was evaporated to about 150 cc. heated to boiling and ammonium hydroxide added until the solution was just alkaline. No precipitate whatever of aluminum was obtained. The collodion flasks were then placed in beakers and the collodion disintegrated by digesting with strong nitric acid on a steam bath over night. Determination of aluminum showed that all of the aluminum contained in the extract had been recovered and that none had diffused through the membrane. This result points directly to the fact that all of the aluminum present in the potassium nitrate extract of the soils under study was present as the hydroxide and not as salts. These results completely confirm the work of Knight, who, as was mentioned earlier in this paper, obtained the same results by dialysis of the potassium nitrate extract of an acid soil.

Before concluding definitely that the aluminum which had been found in the potassium nitrate extracts was present as the hydroxide, it was thought desirable to make a study of the hydrosol of aluminum hydroxide, particularly with reference to its appearance, and behavior in the presence of ammonium hydroxide. Some doubt existed at this time as to whether the hydrosol would not appear quite opalescent, whereas the soil extracts were as clear as distilled water. Furthermore, it was not altogether certain that aluminum in the sol state would be precipitable by ammonium hydroxide. In order, then, to remove any doubts as to the appearance and behavior of the sol in so far as this problem is concerned, certain observations were made on aluminum hydroxide in this condition.

Experiment 2. Properties of the hydrosol of aluminum hydroxide

The procedure followed in the preparation of the hydrosol was that of A. Müller, reproduced in Zsigmondy and Spear's Chemistry of Colloids (16). A solution of aluminum chloride containing 1.124 gm. of aluminum oxide in 50 cc. of water was treated wih ammonium hydroxide, washed as quickly as possible with water, and put into 250 cc. of water in a flask. The whole was brought to a boil, and 20 cc. of N/20 hydrochloric acid added drop by drop. The hydrosol prepared in this manner was only faintly opalescent. A portion diluted with water, however, formed a perfectly clear solution. The hydrosol was found to be neutral to both red and blue litmus paper. On addition of ammonium hydroxide with warming, a gelatinous precipitate of aluminum hydroxide was formed. In view of the similarity in appearance and behavior of the aluminum hydroxide hydrosol with that form of aluminum which was found in the potassium nitrate extracts, together with the fact that the aluminum in the extracts failed to diffuse through the collodion membrane, admits of no doubt as to the form in which aluminum was present in the extracts, namely, the hydrosol of aluminum hydroxide.

Experiment 3. Effect of complete extraction of acidity on nature of aluminum compounds in potassium nitrate extracts

The question now arose as to whether, under the conditions of the extraction with consequent production of equilibrium, sufficient aluminum as salts had been extracted to give a determinable amount of aluminum after dialysis, and whether complete extraction of the soil acidity would tend to modify the character of the aluminum compounds extracted. In order then to extract the total amount of soluble aluminum, the soils, except that from Rhode Island, were shaken as before with normal potassium nitrate. After settling, all the supernatant liquid was removed, replaced with fresh salt solution and shaken again. This process was repeated until titration of 125 cc. of the extract required less than 0.5 cc. of standard sodium hydroxide to neutralize it. It was found impossible to go below this figure on account of the slightly acid reaction of the potassium nitrate solution. Six shakings of 3 hours each with replacement of the salt solution after the first five shakings were found to be necessary to reduce the acidity of the last portions to practical neutrality. A similar series was extracted with distilled water, but because two of

TABLE 5

Aluminum in potassium nitrate extract after complete extraction of acidity of soils

SOIL	ALUMINUM
	lbs. per acre
Gray silt loam	1014
Yellow-gray silt loam	765
Yellow silt loam	802

the extracts persisted in remaining turbid, these water extracts were discarded. The results of the analyses for aluminum in the potassium nitrate extracts, appear in table 5.

A comparison of these results with those received from the single shaking with potassium nitrate reveals the fact that from one and one-half to two times as much aluminum is removed by the successive shakings as with a single shaking, which was to be expected. A very striking comparison, however, is made when the second series of results are compared with those obtained by Mirasol (reproduced in table 3), by leaching the same soils to neutrality with normal potassium nitrate. It should be noted in this connection that the procedure followed by Mirasol was quite different from that used by the writer in that the results of the former were obtained from analysis of the soils before and after extraction, no attempt being made to analyze the extract itself. And herein, undoubtedly, lies the reason for the very high results obtained by Mirasol, for it is highly probable that the percolation of the potassium nitrate through the soils carried with it mechanically a very large quantity of finely divided particles of aluminum hydroxide. Naturally

the hydroxide in this form would not be found in analysis of the extract, but it would reduce enormously the quantity of aluminum in the soil after extraction had been completed. This explanation likewise accounts for the large quantity of aluminum which Mirasol found was removed by leaching with water. None whatever could be found in the extract by the writer in repeating the work in exactly the same manner as Mirasol had done, with the exception that the writer made his analysis of the actual extract rather than of the soil itself. Additional support of this result is given by the fact that the bottom of the bottles receiving the percolate was in each instance covered with a noticeable layer of finely divided material, presumably aluminum hydroxide. More detailed consideration of the water extracts will be given later.

The potassium nitrate extracts of the three soils after complete extraction of soil acidity were now subjected to dialysis by concentrating to small volume and dialyzing in the manner previously described. Here another apparently abnormal result was obtained, for all of the aluminum contained in the extract was found to diffuse completely through the membrane and the total quantity of aluminum in the extract was recovered in the diffused portion. Treating the dialyzate with ammonium hydroxide after digestion with acid failed to give a test for aluminum.

Explanation of the presence of aluminum nitrate in the potassium nitrate extract

The fact that with a single shaking of the soils with potassium nitrate only non-dialyzable aluminum was to be found in the extract, while with complete extraction only dialyzable aluminum was found, can be explained only by assuming that the aluminum hydroxide present in the extract after shaking was converted to aluminum nitrate by the increased acidity which resulted from successive shakings over a long period. It might appear possible that the single extract from the shaking contained aluminum as salts in insufficient quantity to be detected, whereas the complete extraction removed a considerably larger amount. This contention, however, is invalidated by the fact that in the first instance non-diffusible aluminum made up the total aluminum content of the extract, whereas in the second instance the total aluminum of the extract consisted of wholly dialyzable aluminum. This fact necessarily presupposes a conversion of aluminum hydroxide to the nitrate and can hardly be explained on another basis.

Assuming such conversion to have taken place, it became necessary to ascertain whether the conversion had occurred as a result of the increased acidity, caused by the repeated shakings, or whether the concentrating of the 800-cc. aliquots to 150 cc. had increased the hydrogen-ion concentration of the solution to a point which would convert the hydroxide to the nitrate. To settle this latter point, dialysis was repeated with larger collodion flasks which obviated the necessity of concentration, but complete dialysis took place as before, thus eliminating the factor of change in the nature of the aluminum compounds due to manipulation.

If the conclusion is accepted that aluminum salts were not present in the extract after the shaking of 3 hours, but that they were produced as a result of contact between the soil and the extract over a much longer period, then certain fundamental considerations must follow. If aluminum salts are not found in the extract after the shorter period of contact then the salts cannot be the real cause of the acidity of the extract. They are produced in side reactions of the true acidic factors within the soil and diminish rather than increase the acidity of the extract to the extent that they fail to hydrolyze completely. The hydrolysis of soluble aluminum salts, on the basis of this reasoning, cannot be a contributing factor to the acidity of the soils under investigation.

A detailed consideration of the probable process by which aluminum nitrate was produced in these soils, follows. The acid soils being deficient in bases, and because of their rather large content of alumino-silicic acids, alumino-silicates, organic acids and of acid salts in general, withdraw the potassium ion from the neutral salt solution until their capacity for base is satisfied. Those compounds containing aluminum then liberate this ion in proportion to the quantity of potassium absorbed. As the potassium ion is withdrawn from the potassium nitrate, hydrogen ions from the various acids and acid salts within the soil combine with the nitrate ion to form nitric acid. The nitric acid thus produced acts upon the aluminum which is replaced by potassium and forms not aluminum nitrate, as would naturally be expected, but forms the hydrosol of aluminum hydroxide. To assume that soluble aluminum hydroxide is produced under these conditions rather than aluminum nitrate probably appears out of harmony with our usual conception of chemical reactions; yet it is necessary to bear in mind the work of Rose on the formation of hydrated aluminum hydrosols in weak acid solution before the acidity is sufficient to form the normal salt. In the soil, undoubtedly, a series of similar hydrated hydrosols are produced until finally the concentration of nitric acid, increasing slowly by the removal of the potassium ion in the rather slow replacement reaction, reaches a point at which aluminum nitrate is produced. It is necessary to point out that contact of the salt solution with the soil over the period of 2 weeks during which the total extractions were made did not result in increased acidity as measured by titration, but in this period the hydrogen-ion concentrations of each of the extracts rose to a point at which the hydroxide was converted to the nitrate. This is to be explained by the fact that hydrogen ions of the weakly dissociated alumino-silicic acids and organic acids which represent the total acidity of these soils, but which affect only slightly the hydrogen-ion concentrations of the soil, were replaced by potassium. The result was the formation of strongly dissociated nitric acid and a consequent increase in the pH value of the extracts. The data reported in table 6 substantiate this contention in that there is seen to be no increase in titratable acidity in soil extracts which have remained in contact with the soils up to 3 months, yet in this interval there has been a singularly large

increase in the concentration of hydrogen ions in the extracts. The results reported in this table were obtained by shaking 100 gm. of soil with 250 cc. of normal po tassium nitrate solution for 3 hours, titrating 125 cc. immediately after settling and also after standing for 1 and for 3 months. Determinations of the hydrogen-ion concentration of the extracts were made by the colorimetric method of Clark and Lubs (4), at the time of the titration.

Examination of the data presented in table 6 reveals some extraordinary changes in the acidity of the soil extracts during the course of the 3 months' standing. The hydrogen-ion concentrations of the extracts have increased considerably by the third month, pointing strongly to the production of a readily ionizable acid, in this case nitric acid. But much more striking are the changes through which the titratable acidity have passed in this period.

TABLE 6

Total titratable acidity and hydrogen-ion concentration of soil extracts after contact with soil for different periods

SOIL	TIME OF CONTACT OF SALT SOLUTION WITH SOIL	TITRATABLE ACIDITY IN TERMS OF STANDARD ALKALI	HYDROGEN-ION CONCENTRATION
		cc.	*pH values*
Yellow silt loam	24 hours	11.0	4.4
Yellow silt loam	1 mo.	3.0	4.2
Yellow silt loam	3 mos.	10.5	2.8
Yellow-gray silt loam	24 hours	9.7	4.0
Yellow-gray silt loam	1 month	9.3	4.0
Yellow-gray silt loam	3 months	9.3	3.0
Gray silt loam	24 hours	4.3	4.6
Gray silt loam	1 month	0.6	4.6
Gray silt loam	3 months	Not determined	Not determined

It will be observed that the total acidity of the yellow and gray silt loams had decreased to a very marked extent after one month's standing but after the entire period had elapsed the total acidity of the former had returned to the original figures obtained by titration after 24 hours. No such change took place in the extract of the yellow gray silt loam; during the whole period, its acidity remained practically constant. Evidently chemical reactions of considerable complexity had taken place in these extracts to account for the fluctuations in the acidity, and no explanation which might be offered without further study might coincide with the actual changes which took place. Nevertheless, a possible explanation might be suggested at this time which would perhaps stimulate further work along this line. It would certainly seem that some of the active hydrogen ions of the extract had been combined into compounds which removed them from the system either through the passage of

the compounds into the colloidal state, e.g., silicic acid, or it may be that compounds were formed containing hydrogen which ionized to only a slight extent. Either of these possibilities would account for the reduction in acidity after one month. Such a reduction in acidity would naturally affect the hydrogen-ion concentration of the extracts. Whereas, the pH value would normally rise immediately with the conversion of the weakly dissociated soil acids to the strongly dissociated nitric acid, it appears from the data presented that the reduction in total acidity, from whatever cause, has prevented the hydrogen-ion concentration from increasing until some time after one month. After this time had elapsed, however, the constantly increasing concentration of nitric acid succeeded in bringing back into the system the acidic compounds which for some reason had been thrown out. It will be observed that the yellow-gray silt loam suffers no change whatever. Evidently it does not contain to an appreciable extent those compounds which by entering the colloidal or insoluble state reduce the acidity of the extract. Whether the explanation that has been suggested is acceptable or not, does not affect the main point, namely, that there was a very considerable reduction in the total acidity of the soils during the early period and subsequent return to the normal acidity of the extracts. Error in manipulation cannot account for the abnormality since a second series of extracts gave similar results with respect to both titratable acidity and hydrogen-ion concentration.

The extracts which had remained in contact with the soil for 3 months were subjected to dialysis with the result that the aluminum compounds in solution in the extracts diffused through the membrane, showing that in the interval of 3 months conversion of aluminum hydroxide to aluminum nitrate had been effected. It should be noted, however, that under the conditions of the extraction, the production of nitric acid is a reversible reaction. Removal of the products of the reaction then would be expected to accelerate its speed. This is exactly what happened in the complete extraction of the soil acidity by repeated shakings with removal of the salt solution after each shaking replacing it with fresh solution. As a result of this procedure, aluminum hydroxide was converted to aluminum nitrate within 2 weeks (the time required for the extraction), whereas even after 1 month's standing without renewal of the salt solution no such change had taken place. The hydrogen-ion concentration of one of the extracts from complete extraction which happened to be saved, corresponded very closely to the pH value of the same soil after 3 months' standing in contact with the salt solution.

In concluding this discussion of the conversion of aluminum hydroxide to the nitrate in the potassium nitrate extracts, it is necessary to emphasize the fact that the hydrolysis of soluble aluminum salts cannot possibly be a factor contributing toward the acidity of soils in general, the term acidity being taken in its true meaning of the effect of free hydrogen ions and not including a toxic effect apart from that of hydrogen ions. Aluminum salts were not found to occur normally in the soils studied but were produced by the interaction of

the soil acids and the potassium nitrate solution. Hence, almunium salts are produced by soil acids and cannot therefore be a cause of the acid reaction of the soil.

Experiment 4. Aluminum in water extracts

Attention has been previously called to the fact that the water extracts of the soils by repeated shakings were too turbid for use in the determination of aluminum. Any attempt to clear the extracts by flocculation of colloidal material, of course, would precipitate aluminum in the hydrosol state. Hence, percolation of the soil with distilled water was resorted to in order to obtain perfectly clear extracts. Five kilograms of each soil was placed in pots of that capacity and leached with distilled water until a 125-cc. portion of the percolate required not more than 0.2 cc. of standard alkali to neutralize it. Approximately 10 liters of water was required by each soil to reduce its acid reaction to neutrality.

Analysis of the water extracts for aluminum was made by evaporating aliquot portions to dryness, allowing the beakers to remain on the steam bath over night to dehydrate the silica, digesting the residue for 1 hour on the bath with 5 cc. of concentrated nitric acid, diluting, and after filtering off the silicia, heating to boiling and treating with ammonium hydroxide in the presence of 2 gm. of ammonium chloride to faint alkalinity. No precipitate whatever formed even when 5-liter aliquots were taken of the total volume of 10 liters of each extract. When it is considered that the total quantity of soil extracted in each case was 5000 gm.; further that there is no reason why any nitrate, sulfate or chloride of aluminum should have failed to be removed by the water had they been present in the soil, the conclusion may be drawn with assurance that soluble aluminum was totally absent from these soils despite the fact that Mirasol has reported between 21,000 and 33,000 pounds of aluminum to have been removed from the same soils by water. The explanation of this discrepancy has been made in connection with the discussion of aluminum in potassium nitrate extract, namely, that these figures reported by Mirasol were not secured by actual analysis of the extracts, but that they represent the loss in total aluminum of the soils after percolation had been accomplished. It was further suggested that the liquid passing through the soil had removed mechanically very fine particles of aluminium hydroxide to which the loss in aluminum may be ascribed. Mirasol, however, does report results from the actual analysis of the water extracts for aluminum. These results are reproduced in table 7.

These results, however, if calculated on the acre basis, vary widely from the results reported by him from analysis of the soils before and after percolation. For instance, selecting the figure given for aluminum in the first 4 liters of the extract of the yellow gray silt loam, namely 105.2 gm. and calculating this in terms of pounds per acre (16 liters of water was the total volume used in leaching the soil), assuming 5000 gm. to be the capacity of the pot used, we

arrive at the figure of 168 pounds per acre; whereas calculation from the results obtained indirectly, i.e., by analysis of the soil before and after percolation, shows that 33,400 pounds per acre had been removed. The figure 168 pounds as a matter of fact is much too large as it is computed from the quantity of aluminum in the first 4 liters which contained considerably more aluminum than the succeeding volumes of water.

It is now necessary to explain the reason for the discrepancy in the results of Mirasol and of the writer in direct analysis of the water extracts. Mirasol does not give his method for the determination of aluminum in the water extracts, so it may be presumed that he disregarded the possible presence of soluble silica in the extracts, treating with ammonium hydroxide to precipitate aluminum directly after evaporation, instead of evaporating the extracts to dryness, dehydrating and removing the silica with subsequent treatment with ammonium hydroxide. It would seem possible then that the precipitate that he obtained with ammonia was not aluminum hydroxide but silicon hydroxide. In order to obtain experimental evidence bearing on this point, the writer evaporated 4 liters of each of the extracts to 200 cc. and treated with

TABLE 7

Analysis of water extracts as reported by Mirasol

SOIL	ALUMINUM
	mgm.
Yellow silt	88.9
Yellow-gray silt loam	105.2
Gray silt loam	75.5

ammonium hydroxide, white gelatinous precipitates being formed in each case. One of the precipitates was pure white, the others were tinged somewhat by ferric hydroxide. Boiling these precipitates with strong sodium hydroxide failed to dissolve them. Even boiling with fairly strong acid brought them into solution only quite slowly. The behavior of these precipitates with acid and alkali should remove any doubt that they were not aluminum hydroxide.

Resuming further consideration of Mirasol's data concerning the presence of aluminum in water extract, it is necessary to say first that it is utterly impossible that all of the aluminum which Mirasol succeeded in extracting from the soil by water was present as salts of the various acids. By calculation of the amount of aluminum that would be combined with the total quantity of negative ion in the extract, assuming for the time that all of the acid ions are present as aluminum salts, it is possible to approximate the maximum quantity of aluminum that might be contained in the extract as salts. This figure compared with the total quantity of aluminum present gives the ratio of aluminum as salts to the total aluminum content. This idea has been carried out with results that appear in table 8. All of the data with the

exception of the analysis of chloride and sulfate, which were carried out by the writer, are taken from Mirasol's report of his work.

A comparison of the maximum amount of aluminum which could be combined with the total quantity of acid ions, leaving the silicate out of consideration, demonstrates at once the extremely small proportion of aluminum that could be present as salts. But we know from the principles of water analysis that the acid ions are not linked with aluminum but with calcium, magnesium, potassium and sodium. All bases, in excess, are assumed to be present as hydroxides.

In no case in water analysis, to the knowledge of the writer, are acid ions, under normal conditions, ever assigned to aluminum. The only alternative to account for the large amounts of aluminum is to ascribe it to the presence of aluminum hydroxide. The writer, of course, does not lose sight of the fact that aluminum hydroxide will be generally admitted to be present in the

TABLE 8

Acid ions in soil solutions extracted by water, with their aluminum equivalent

IONS	GRAY SILT		YELLOW-GRAY SILT		YELLOW SILT	
	Acid ions	Aluminum equivalent	Acid ions	Aluminum equivalent	Acid ions	Aluminum equivalent
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Nitrate	18	3	26	4	62	9
Chloride	152	38	212	53	112	28
Sulfate	422	79	598	112	459	86
Phosphate	*	*	*	*	13	3
Total		120		169		126
Total aluminum estimated	21,400 lbs.		33,400 lbs.		32,200 lbs.	

* Amount within error.

water extract of soils; Mirasol, in fact, mentions its probable occurrence in the soil solution. The writer also recognizes the possibility of its presence being a potential source of toxic aluminum, but he does not admit the correctness of grouping it with aluminum in the form of salts under the head of active aluminum, i.e., aluminum that is toxic to plants. It follows, therefore, that the total aluminum which may be found in water extracts cannot be taken as a measure of toxic aluminum since the latter occurs to the best of our knowledge only as salts which, as has been shown, are not likely to be present in soils in significant amounts.

THE PRODUCTION OF SOLUBLE ALUMINUM IN THE SOIL BY BACTERIAL ACTIVITY

Thus far in this paper no data have been adduced which indicate that the rise of aluminum salts within the soil might contribute towards its acidity. It has been shown that aluminum salts produced by purely chemical reactions

cannot possibly augment the acid reaction of the soil. It is now necessary to consider whether soil acidity might be increased by the hydrolysis of aluminum salts produced biochemically, namely, by nitrification and by sulfofication. Mirasol has emphasized the former process as being the foremost factor in the production of soluble aluminum, pointing out that in absence of a more suitable base, aluminum may serve as the base in nitrification with the production of considerable quantities of aluminum nitrate. That this process may take place to any extent, however, may be doubted in view of the fact that nitrifying bacteria are extremely sensitive to an acid medium which would rapidly be brought about by the hydrolysis of aluminum nitrate, if formed. Certainly nitrification could not go on appreciably under such conditions. Nevertheless, it was deemed desirable to study this question experimentally.

Experiment 5. Nitrification as a factor in the production of soluble aluminum

This experiment was performed by determining the amount of nitrate in incubated nutrient media which contained no free base which might neutralize nitric acid except aluminum hydroxide and aluminum phosphate.

TABLE 9

Nitrate production in liquid cultures

TREATMENT OF NUTRIENT MEDIUM BEFORE INOCULATION WITH SOIL INFUSION	NITRATE NITROGEN	
	After 4 weeks	After 6 weeks
	mgm.	*mgm.*
$(NH_4)_2SO_4$	1.1	1.0
$(NH_4)_2SO_4$ and $Al(OH)_3$	0.6	0.9
$(NH_4)_2SO_4$ and $AlPO_4$	0.5	0.5
$(NH_4)_2SO_4$ and $CaCO_3$	5.5	5.3

The nutrient medium contained per liter of distilled water, 1 gm. of K_2HPO_4, 0.2 gm. of $MgSO_4$, 1 drop of 10 per cent $FeCl_3$, 1 gm. of NaCl and a very small amount of $CaCl_2$. Twenty-five cubic centimeters of the medium was poured into 500 cc. Erlenmeyer flasks, each of which received in addition sufficient standard $(NH_4)_2SO_4$ solution to provide 10 gm. of nitrogen. Aluminum hydroxide and phosphate were added to separate series of flasks in amounts sufficient to neutralize all of the nitric and sulfuric acids that might be produced, plus a slight excess. The flasks were then inoculated with 1 cc. of a soil infusion made by shaking 100 gm. of a black clay loam soil with 200 cc. of water and allowing the supernatant liquid to stand until most of the soil particles had settled. Incubation at 30° was allowed to continue for 4 and for 6 weeks. At the end of these intervals, the contents of the flasks were analyzed for nitrate with results as given in table 9 as averages of triplicates.

From the data contained in the table there does not seem to be any likelihood of aluminum replacing calcium as an available base in nitrification. The experiment, however, probably does not admit of a definite conclusion on this point, since it might be that in a much longer period of incubation the aluminum compounds would slowly be attacked and a measurable quantity of nitrate would be formed. In addition, there is a possibility that if nitrification were intiated by a slight amount of carbonate, aluminum would carry on the process.

Experiment 6. The production of soluble aluminum in the soil by the process of sulfofication

It will be recalled that reference was made earlier in this paper to the fact that Ames and Boltz (2) report aluminum as having been rendered soluble in the process of sulfofication. As their experimental procedure did not discriminate between the two forms in which aluminum may be produced in the soil, i.e., as the hydroxide or as salts, it became necessary in order to study this problem to induce strong sulfofication in a soil and then to dialyze the extract as in the previous experiments. Accordingly, 100-gm. portions of the yellow gray soil were placed in tumblers, 0.5 gm. of sulfur was added, 0.8 gm. of dried blood, and finally enough precipitated aluminum hydroxide to double the aluminum content of the soil. Water was then added to optimum moisture content and the tumblers incubated at room temperature for 2 months, water being added from time to time to keep the tumblers at a fixed weight. At the end of the incubation period the contents of each tumbler were transferred to a 400-cc. shaker bottle, 200 cc. of distilled water added and the mixture shaken for 1 hour. After the suspended material had settled aliquot portions were drawn from each bottle, sulfate being determined from two portions, the remainder being dialyzed in the manner that has been previously described. Very strong oxidation of sulfur was found to have taken place, the sulfuric acid formed being sufficient to increase the pH value of the soil extracts from 4 to 3. Under such conditions, it was not surprising that conversion of aluminum hydroxide to sulfate took place as was demonstrated by dialysis. It is hardly necessary to point out that the aluminum sulfate formed in this manner could not possibly have been a factor in increasing the acidity of the soil extracts since this was of course due solely to the sulfuric acid formed.

Experiment 7. The influence of aluminum salts on ammonification and nitrification

Although thus far in the experimental work that has been reported in this paper, no evidence has been adduced that has indicated the presence of aluminum salts in acid soils under normal conditions; yet we are confronted with the results of the work of Hartwell and Pember (11), which seems to admit of no other conclusions than that aluminum was the toxic factor which account-

ed for the unique difference in the response of rye and barley to identical soil conditions. Other work which hardly need be reviewed at this time points quite clearly to the harmful influence of those salts in acid soils. Acid soils under a given set of conditions, as in sulfofication, may favor the production of aluminum salts; and, because of their very high toxicity, plant growth might be seriously affected, even though the absolute quantity of salts produced at any one time may be very small.

With these considerations in mind and in view of the lack of data in the literature bearing on the influence of aluminum salts on ammonifying and nitrifying organisms, it was deemed advisable to study to what extent the soil flora concerned in nitrate production reacts toward toxic aluminum. Data which would demonstrate the relative toxicity of the aluminum salts likely to occur in the soil, also seemed of sufficient importance to warrant some attention being given to this phase of the subject. Furthermore, if aluminum was found to inhibit seriously the normal functioning of the nitrifying organisms, it would be of considerable practical importance to ascertain the relative value of certain common fertilizing materials for inactivating the toxic aluminum. A description of the experiments devised to throw light on these points follows.

The soil selected for this work was a slightly acid brown silt loam from the University South Farm. Its lime requirement according to the Hopkins method was 300 pounds per acre. It had a high ammonifying and nitrifying power and for this reason was more suitable than any of the acid soils used in connection with the work on extraction of aluminum. An obvious objection to the use of a soil with such a slight degree of acidity is that aluminum applied to it in the form of salts would be precipitated until the acidity of the salts had increased the hydrogen-ion concentration of the soil beyond the point at which aluminum is thrown out of solution. It was planned, however, to apply the aluminum salts over so wide a range of concentrations that no difficulty would be experienced in bringing about, for the duration of the experiment at least, the presence of soluble aluminum in the soil. Time did not permit a complete chemical analysis of the soil, but for the sake of information an analysis is presented in table 10 which represents the average chemical composition of the soil of the same type in the county from which the sample was taken. These data were obtained from the Soil Report of Champaign County, Illinois and was prepared by the University of Illinois.

One-hundred-gram portions of the soil were placed in tumblers and mixed with organic matter consisting of a mixture of alfalfa and sweet clover residues and furnishing the nitrogen equivalent of 200 pounds per acre. The nitrate, chloride, sulfate and phosphate of aluminum were then applied to separate series in chemically equivalent amounts. The concentrations of salts are indicated in table 11. With the exception of the phosphate, all of the salts were added in solution. Water was added in amounts such that the total volume of liquid applied, that is water and the aluminum salt solution,

was 25 cc., the optimum moisture content of the soil. This moisture content was maintained as nearly as possible during the incubation period by adding from time to time the amount of water lost from several weighed tumblers.

TABLE 10

Composition of brown silt loam of Champaign County

COSTITUENT	AVERAGE AMOUNT FOUND PER ACRE OF TWO MILLION POUNDS
	lbs.
Total nitrogen	4,670
Total phosphorus	1,060
Total potassium	35,430
Total magnesium	9,550
Total calcium	10,680

TABLE 11

Concentrations of aluminum salts used and field rates of application

CONCENTRATION NUMBER	FRACTION OF MOLECULAR WEIGHT PER 100 GM. SOIL	$Al(NO_3)_3$	$AlCl_3$	$Al_2(SO_4)_3$	$AlPO_4$
		lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
1	156×10^{-7}	67	42	107	38
2	625×10^{-7}	266	167	427	153
3	25×10^{-5}	1,064	669	1,709	610
4	1×10^{-3}	4,255	2,688	6,836	2,440
5	4×10^{-3}	17,019	10,670	7,348	9,759

TABLE 12

Ammonia production in soil treated with aluminum salts after incubation, per acre in pounds

CONCENTRATION NUMBER	$Al(NO_3)_3$		$AlCl_3$		$Al_2(SO_4)_3$		$AlPO_4$	
	1 week	2 weeks	1 week	2 weeks	1 week	2 weeks	1 week	2 weeks
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
Check	24	23	24	23	24	23	4	23
1	29	16	29	20	36	26	34	28
2	27	16	30	16	32	24	30	24
3	40	18	30	19	32	21	28	16
4	36	20	39	58	26	12	32	24
5	33	34	40	36	21	0	50	23

The experiment consisted of four series, namely ammonia production in 1 week and in 2 weeks, and nitrate production in 1 and in 2 months of incubation. The results as reported in tables 12, 13 and 14 are averages of the analyses of duplicate tumblers. Whenever difficulty was met in obtaining

satisfactory checks that section of the work was repeated. Ammonia was determined by distilling with magnesium oxide, nitrate by boiling off ammonia with sodium peroxide and distilling with Devarda alloy.

TABLE 13

Nitrate production in soil treated with aluminum salts, after 1 month's incubation

NUMBER	NITRATE FOUND AFTER TREATMENTS INDICATED					
	$Al(NO_3)_3$			$AlCl_3$	$Al_2(SO_4)_3$	$AlPO_4$
	Total found	Applied as $Al(NO_3)_3$	Found in excess of that applied.			
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Check	126		126	126	126	126
1	185	12	173	33	141	90
2	84	48	36	33	111	135
3	174	192		96	90	135
4	173	768		48	72	174
5	159	2,072		54	174	204

TABLE 14

Nitrate production in soil treated with aluminum salts, after 2 months' incubation

NUMBER	NITRATE FOUND AFTER TREATMENTS INDICATED					
	$Al(NO_3)_3$			$AlCl_3$	$Al_2(SO_4)_3$	$AlPO_4$
	Total found	Applied as $Al(NO_3)_3$	Recovered			
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Check	54		54	54	54	54
1	82	12	72	72	110	90
2	90	48	42	66	99	60
3	114	192		72	62	48
4	201	768		72	93	78
5	336	3,072		60	76	Lost

Discussion of results from ammonification and nitrification

Considering first the ammonia determinations after 1 week's incubation, we may say that no toxic effect is to be noted; as a matter of fact, a considerable stimulation seems to be the rule even in the very high concentrations. No great depression of ammonia takes place after 2 weeks except in the highest two concentrations of aluminum sulfate and in a few other cases. These variations may be explained by the fact that nitrate production was stimulated at these particular concentrations, a fact which is borne out in part by the nitrate data.

Turning now to the data of nitrate production after 1 month we find as might have been predicted from our knowledge of the sensitivity of the nitrate and nitrate organisms to acidity that, with the exception of the phosphate in which there is stimulation, there is a general decrease in nitrate formed with increasing concentrations of the salt. The high result in the fifth concentration of aluminum sulfate is to be explained by a disturbance in the system brought about by the high acidity. No doubt the aluminum has exerted its toxic effect as in the other concentrations, but this effect is masked by the dissolving out of some elements to which the bacteria readily responded. The results from the applications of aluminum nitrate are altogether unsatisfactory because none of the nitrate applied in the higher concentrations could be recovered after incubation. Apparently the conditions were favorable for the rapid development of a nitrate consuming flora, or denitrification may have taken place. It was predicted that the phosphate would probably not exert a toxic effect, and it was incorporated in the series partly with the idea in mind of finding whether the nitrifying bacteria would respond to quite insoluble phosphate. Then, it was reasoned, if the phosphate ion is removed by the organisms, the free aluminum ion may have opportunity to exert a toxic effect by combining with an acid radical. The phosphate, it would seem, is quite available to bacteria.

The nitrate results after 2 months' incubation are quite striking in that they demonstrate the fact that soluble aluminum is slowly precipitated or thrown out of action in some way by the soil even in the very highest concentrations. It is realized, as has been indicated before, that a soil of this character would likely dispose of considerable active aluminum by precipitation, and for this reason the objection might be raised that the results are not applicable to normally acid soils. Yet, if this soil is able to dispose of some 27,000 pounds of aluminum sulfate and 10,000 pounds of aluminum chloride, it would seem that a more acid soil could inactivate the much smaller quantities of aluminum salts that it is likely to contain.

For some unknown reason the magnitude of the results from the 2 month's incubation is lower than that from the incubation of a single month. Possibly denitrification resulted from an excess of water that might have been added during the course of the incubation period, or it may be that after the maximum quantity of nitrate had been produced a considerable quantity of nitrate was utilized by a strong nitrate consuming flora. The general trend of the data, however, is not affected by the rather low production of nitrate in the longer incubation period.

Experiment 8. The influence of fertilizing material on the precipitation of aluminum

The final experiment to be reported has to do with the relative efficiency of certain fertilizer materials, namely calcium carbonate, monocalcium phosphate and tricalcium phosphate in diminishing the toxicity of aluminum.

Each of these compounds was mixed with soil in the amounts necessary to precipitate the aluminum from aluminum chloride which was added to the soil in the same concentrations that were employed in the previous experiments. The precipitation of the aluminum from aluminum chloride was assumed to take place according to the following equations:

$$2\,AlCl_3 + 3\,CaCO_3 = 2\,Al_2O_3 + 3\,CaCl_2 + 3\,CO_2$$
$$2\,AlCl_3 + 3\,CaH_4(PO_4)_2 = 2\,AlPO_4 + 4\,H_3PO_4 + 3\,CaCl_2$$
$$2\,AlCl_3 + Ca_3(PO_4)_2 = 2\,AlPO_4 + 3\,CaCl_2$$

Incubation was allowed to take place for 1 month. The results with tricalcium phosphate were unsatisfactory, so a second series was incubated.

TABLE 15

Effect of carbonate and phosphates in inactivating soluble aluminum as measured by nitrate production

CONCENTRATION NUMBER	$AlCl_3$	$AlCl_3 + CaCO_3$	$AlCl_3 + CaH_4(PO_4)_2$
	lbs. per acre	*lbs. per acre*	*lbs. per acre*
Check	126	126	126
1	63	186	78
2	63	183	108
3	96	153	102
4	48	172	84
5	54	87	36

TABLE 16

Effect of tricalcium phosphate in inactivating soluble aluminum as measured by nitrate production

CONCENTRATION NUMBER	$AlCl_3$ ALONE	$AlCl_3 + Ca_3(PO_4)_2$
	lbs. per acre	*lbs. per acre*
Check	120	120
1	108	126
2	93	105
3	66	92
4	105	99
5	75	30

The results from this second series with tricalcium phosphate should be compared with the results from the aluminum chloride series which accompanied it, rather than with the results of the first series. Chemically pure chemicals were used.

The superiority of calcium carbonate over the two phosphates precipitating aluminum as measured by nitrate production is apparent at once. The monocalcium phosphate is likewise to be preferred to the tricalcium phosphate for this purpose.

SUMMARY

The experimental work that has been reported, together with the interpretations of which it admits, have established conclusively the fact that aluminum salts were not present in the acid soils which were used in this investigation. Although aluminum nitrate was found in the potassium nitrate extract of the soils after complete extraction of the acidity had been accomplished, this fact by no means establishes the normal occurrence of aluminum salts in these soils. The very fact that not a trace of soluble aluminum was found in the water extracts is conclusive evidence of its absence, as there is no reason why salts of aluminum, if present, should not have been extracted by distilled water. It has been shown further that even if the total content of acid ions within the soil were combined with aluminum, even this impossible condition could account for only an insignificant quantity of total aluminum extracted.

Soluble aluminum salts may be produced from aluminum hydroxide in acid soils by the action of the mineral acids formed by removal of the basic ion of sulfates, chlorides and nitrates. The basic ions replace aluminum in certain soil minerals, the aluminum coming into solution as the hydroxide. With increasing hydrogen-ion concentration of the soil solution, brought about by the production of highly ionized acids by withdrawal of the bases from salts, a point is reached when aluminum hydroxide in solution is converted into soluble aluminum salts. Since the hydrolysis of these salts cannot increase the acidity of the soil beyond the degree of acidity existing at the time of their formation, the conclusion may be definitely drawn that aluminum salts are not a factor in the acidity of soils, taking the term acidity to refer to the effect of free hydrogen ions and not including a toxic effect due to other causes. Rather than causing an acid condition in soils, aluminum salts are themselves produced by the acidity of the soil, and hence cannot contribute toward it.

It has been shown that the presence of soluble aluminum salts stimulates ammonification while nitrification proper is affected adversely with increasing concentration of the salts. This inhibitive effect, however, is obtained in the soil used only for a relatively short time, perhaps no longer than a month. After 2 month's incubation it is striking to note that, with nitrate production as the criterion, the soluble aluminum had been rendered inactive. Calcium carbonate was shown to be more effective than either monocalcium or tricalcium phosphate in precipitating aluminum, as measured by nitrate production.

CONCLUSIONS

1. Soluble aluminum salts were not present in the acid soils used in this investigation.

2. Aluminum salts, although perhaps occurring in some acid soils, do not contribute to their total acidity, but are themselves produced by the action of the soil acids.

3. Aluminum salts are stimulating to ammonifying organisms, but act adversely upon nitrate bacteria in soil. This effect, however, is temporary only, as an acid soil seems to have considerable capacity for inactivating toxic aluminum.

4. Calcium carbonate is the most effective material, in reducing the toxic action of aluminum salts on nitrification.

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STUDIES OF SULFUR OXIDATION IN SULFUR-FLOATS-SOIL MIXTURES[1]

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EFFECT OF AERATION

The process of mixing rock phosphate, sulfur and soil according to the Lipman formula for the purpose of converting the insoluble into soluble phosphates, is based upon the phenomenon of the oxidation of sulfur by microörganisms. The sulfuric acid produced reacts with the tricalcium phosphate forming the secondary and primary salts. These are soluble in water and in neutral ammonium citrate and thereby readily available for plant use. This process may be expressed in terms of chemical reactions and studied from an empirical standpoint. The equations are:

$$2S + 2H_2O + 3O_2 = 2H_2SO_4$$
$$Ca_3(PO_4)_2 + H_2SO_4 + 2H_2O = Ca_2H_2(PO_4)_2 + CaSO_4 \cdot 2H_2O$$
$$Ca_2H_2(PO_4)_2 + H_2SO_4 = CaH_4(PO_4)_2 + CaSO_4$$

Examining the first equation the outstanding feature is the consumption of large amounts of oxygen in the process of oxidation of sulfur. It is, therefore, suggestive to assume that the microörganisms concerned in the process are strictly aerobic and responsive to a higher oxygen tension. Both of these questions have been the subject of study of Lipman and McLean (8, 9). The aerobic nature of the microörganisms in question has been definitely established. The oxygen tension has also been studied but not to any great extent and the limits of oxygen supply have not been established. It was with this in mind that the following work was conducted.

Mixtures of 50 gm. of floats, 25 gm. of flowers of sulfur and 25 gm. of dry soil were made, moistened to within 50 per cent of the total water-holding capacity, and placed in 250 cc. wide-mouth bottles. Each bottle with the mixture was inoculated with a 5-cc. infusion made by mixing 10 gm. of floats-sulfur-soil compost known for its efficacious oxidizing power with 50 cc. of water.

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[2] The author wishes to acknowledge his appreciation of the enthusiasm and guidance of Dr. Jacob G. Lipman.

Nine bottles, each containing this same mixture, were arranged in series and aerated as shown in figure 1. *A* represents a flask with ordinary tap water. *B* is the first bottle containing the mixture, *C* the second, etc. Air enters bottle *A*, through tube *T*, passes through the water, becomes somewhat saturated and passes to bottle *B*. Tube *D* has at its lower end, a bulb, *b*, $\frac{3}{4}$ inch in diameter. The stream of air enters the mixture through a dozen or more pin holes in this bulb, passes through the mixture and leaves the bottle *B* through tube *E* to enter bottle *C* and repeat the operation. The essentials of this aeration apparatus have been taken from Folin's (4) aeration apparatus for the determination of ammonia. Suction was accomplished by an apparatus used at this station and described by Neller (10).

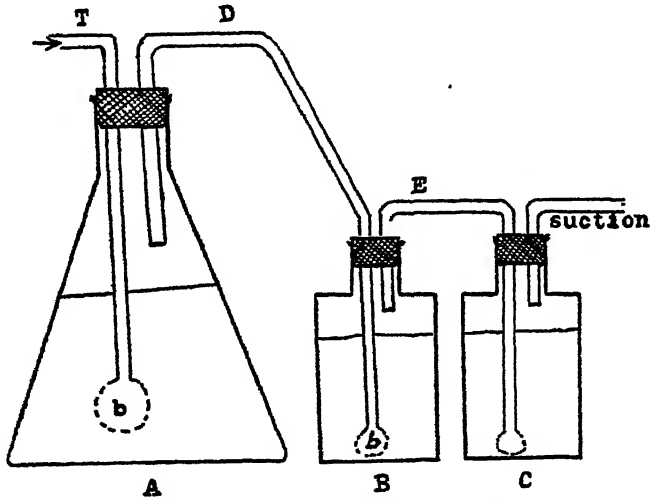

FIG. 1. DIAGRAM SHOWING METHOD OF AERATION

Two bottles served as controls which were, therefore, not aerated. Each bottle throughout the aeration experiment was weighed weekly, water was added to make up for loss through evaporation and also for water taken up in the oxidation of sulfur as shown in the equation:

$$2S + 2H_2O + 3O_2 = 2H_2SO_4$$

It was found that the aerated bottles near the water bottle *A*, lost more water than those at the end of the system near the suction connection. This made it necessary to change the order of the bottles two or three times a week in order to give all the bottles a fairly even chance and thus eliminate a variable. Besides the moisture factor, the question of amount of oxygen was involved in the changing of the bottles from one end of the system to the other. As the air proceeds toward the last bottle, the oxygen in it is used up by the microörganisms. The greater the distance from the source of air, therefore, the less is the amount of oxygen supplied to the microörganisms. It is hoped in

future work, to measure the incoming and outgoing oxygen and thus determine the oxygen requirements of the sulfur-oxidizing organisms. From time to time, the bottles were sampled for determination of hydrogen-ion concentration and phosphorus soluble in neutral ammonium citrate. The colorimetric method as described by Clark (3) was used for the pH determinations and the official method (11) for the phosphorus determinations. The results of the experiment are shown in table 1.

A glance at the figures in table 1, shows that there was, after 100 days, 6 per cent more of the citrate-soluble phosphorus, in the aerated mixtures than in the non-aerated mixtures. After that time the aeration had no effect and the difference between the two series remained about the same.

TABLE 1

Comparison of aerated and non-aerated sulfur-floats-soil mixtures

AGE OF CULTURES	AERATED SAMPLES*		NON-AERATED SAMPLES†		EXCESS OF PHOSPHORUS MADE AVAILABLE BY AERATED MIXTURE OVER NON-AERATED
	Acidity	Phosphorus made available	Acidity	Phosphorus made available	
days	*pH*	*per cent*	*pH*	*per cent*	*per cent*
0	6.4	7.5	6 4	7.5	0.0
10	4.2	12.5	4.8	9.6	2.9
25	4.0	19.6	4.2	15.0	4.6
80	2.8	33 2	2 8	28.8	4.4
100	2.6	36 3	2.8	30.0	6.3
120	2.6	39.8	2.8	33.9	5.9
130	2.6	41.7	2.6	35.7	6.0
150	2.6	46 8	2.6	41.0	5.8
180	2.4	49.9	2.6	44.4	5.5

* Samples, taken in duplicate, were representative of the material in the entire series of nine bottles.

† Samples representative of material in both control bottles.

The same phenomenon was observed in the reaction. In analyzing the sulfur oxidation equations from a physico-chemical viewpoint, it must be remembered that the velocity of a reaction is proportional to the product of the active masses of substances involved. In this case, the active masses of oxygen has been increased through aeration and, of course, there should be an increase in oxidation. There are, however, other factors beside mass that enter a reaction of this nature. It must be remembered that the microörganisms must come in contact with the sulfur in order to oxidize it and that they have need of great masses of oxygen. Thus, the increased oxygen supply is of direct benefit to the microörganisms. It is known that the food supply in any medium brings forth competition among the different groups of microörganisms. Any condition that will favor a certain group of organisms will place this group in an advantageous position at the expense of the others. In the case of non-aeration, the oxygen supply in the beginning was used up by

the different groups, outside the sulfur bacteria, and the sulfur-oxidizing organisms were deprived of their required oxygen. This will explain also why after the reaction reached a certain point, no advantage has been derived from aeration. In the beginning, many other species of organisms were present in the mixtures as shown by the plate method. But when the reaction went

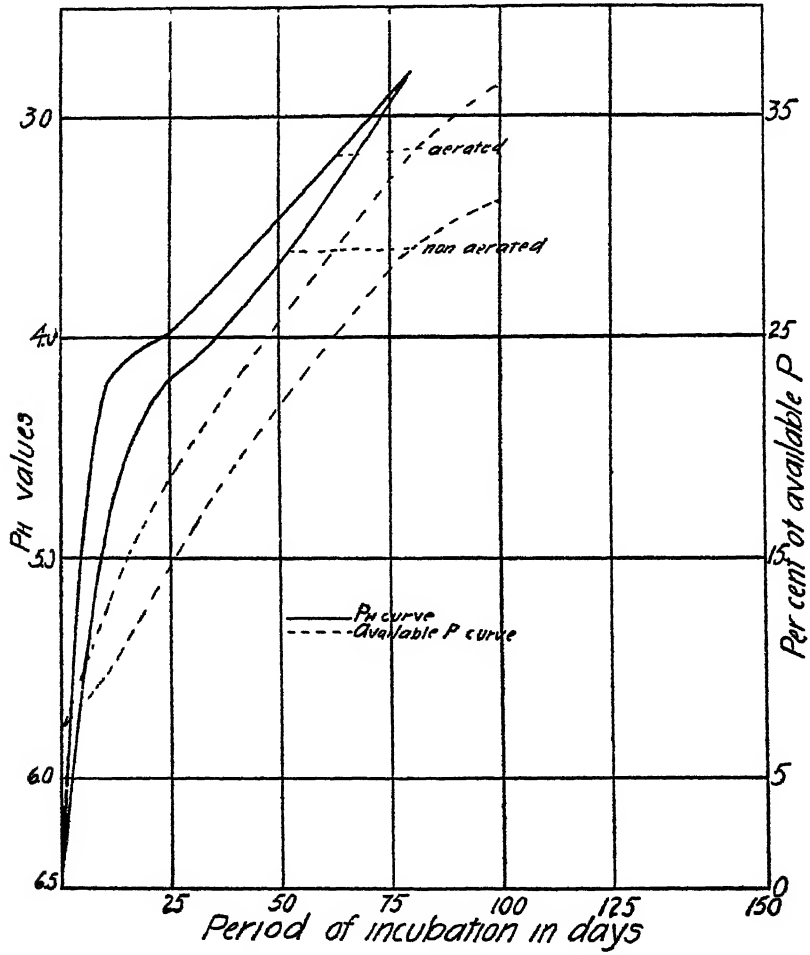

FIG. 2. CURVES SHOWING RELATION OF AERATED AND NON-AERATED CULTURES EXPRESSED BY THE PER CENT OF AVAILABLE PHOSPHORUS AND REACTION

down to a pH 2.8 no bacteria appeared on the plates; as a matter of fact no organisms, except a fusarium, were present. Microscopic examinations showed the typical minute rod-shaped bacteria with rounded ends. Thus the sphere of action at a pH 2.8–2.6 is left to the sulfur-oxidizing bacteria only.

Until the pH of the non-aerated mixtures reached the value 2.8, their bacteria were the least active, as seen from the table 1. As soon, however, as

the reaction was reduced to a pH 2.8, these non-aerated mixtures produced soluble phosphates as fast as the others. The normal supply of oxygen as found in the atmosphere seems to be sufficient at the particular reaction under the conditions of the experiment. Thus the limits of oxygen tension must be taken into consideration. In composting rock phosphate and sulfur, depth of layer is of prime importance, from the standpoint of oxygen supply especially until the reaction goes down to a pH 2.8. It may be deduced from what has been said about the relation of aeration to reaction that it is essential in the composting process to impart to the surrounding medium a reaction as expressed by a pH value of 2.8. That this is not so will be pointed out later in discussing the question of the effect of reaction on the speeding up of the process of sulfur oxidation.

While weighing the bottles to measure the loss of water by evaporation, it was noted that after 80 to 100 days the mixtures gained in weight instead of losing, even though they dried up. The reason for this was not clear at first but the writing out of the equation representing the reaction solved the difficulty.

$$2\ S + 2\ H_2O + 3\ O_2 = 2\ H_2SO_4 + 282\ Cal.$$

Thus two atoms of sulfur need two molecules of water and three molecules of oxygen to make up two molecules of sulfuric acid. The water serves a double purpose, that of supplying water for the sulfuric acid formed and that of keeping the mixtures at an optimum moisture condition for the development of the organisms. The gain in weight may be calculated from the equation:

$$2\ S + 3\ O_2 + 2\ H_2O = 2\ H_2SO_4$$
$$64 + 48 + 36 = 196.$$

Thus for sixty-four units of sulfur we get one hundred ninety-six units of sulfuric acid, or for every gram of sulfur we get 3.02 gm. of sulfuric acid, a gain in weight of more than 2 gm. for every gram of sulfur oxidized. This makes the moisture problem in the composting of sulfur and floats more complicated, since at any moment of the reaction, the increment of sulfuric acid produced determines the moisture content. The moisture content becomes a function of the sulfur oxidized. In order to determine accurately the loss of moisture, a determination has to be made, but this is a tedious method and a more simple one may be used. It consists in determining the total sulfates by the 1 per cent HCl method described by Brown and Kellog (2) and calculating the amount of sulfur oxidized. The equation of sulfur oxidation may be then used for the calculation of water of constitution of the sulfuric acid formed. The amount of water lost by evaporation may be determined by keeping a control with the same mixture, leaving out the sulfur, and substituting sand for it.

Loss of weight by the control will give the moisture lost by evaporation. One other point must be considered in a theoretical consideration of water con-

sumed in the process of sulfur oxidation, namely, the water of crystallization of the gypsum formed in the reaction of the sulfuric acid on the ground rock phosphate. Two molecules of water are tied up with one molecule of calcium sulfate. The latter may also be calculated from the equations given previously.

INFLUENCE OF INITIAL REACTION

It has been pointed out that aeration ceased to be a factor in the mechanism of sulfur oxidation after the mixtures reached a pH value of 2.8.

In an earlier paper, Lipman and Joffe (7) have reported the results of an experiment planned to study the influence of the initial reaction on the oxidation of sulfur. They concluded that under the conditions of their experiment there is no advantage in starting with a relatively high hydrogen-ion concentration through conditions of sulfuric acid. To see the effect of reaction on the oxidation of sulfur in mixtures as in the aeration experiment was the primary object of the experiment recorded. The experiment reported here was carried out under entirely different conditions.

PROCEDURE

Mixtures were prepared in the same way as for the aeration experiment. Tumblers were used instead of bottles. They were kept at room temperature and acidified as indicated in table 2.

Each tumbler received 20 cc. of water and 5 cc. of infusion as in the aeration experiment. The pH determinations were made several hours after the addition of the acid.

The addition of the acid did not bring the reaction down to a pH 2.8. This can be explained by the composition of the mixture. Fifty per cent of it was rock phosphate, which easily removed the hydrogen ions from the sphere of reaction. The twenty-five grams of soil undoubtedly absorbed or adsorbed most of the acid, withstanding the "attacks" of the hydrogen ions through the buffers present in the soil. Still the total acidity increased and exerted some influence. Table 3 records the developed reaction and the availability of the phosphates for a period of four months. It brings out some interesting features of the effect of reaction on the oxidation of sulfur.

The results are not striking and not absolutely conclusive. The indications, however, are interesting. It seems that small additions of sulfuric acid have a beneficial effect on the process of sulfur oxidation in sulfur-floats-soil composts. The first three cultures through the whole period of incubation showed consistently more activity than the remainder. The reaction and also the percentage of soluble phosphates are the expressions of these activities. The control mixtures were favored by conditions fully as much as those treated with larger amount of acids, perhaps even a little more, if the chemical effect of the initial addition of sulfuric acid to the others is considered. Of course, differences are due to the additions of sulfuric acid, but how and why remains

TABLE 2

Treatment of sulphur-floats-soil mixtures

NUMBER OF TUMBLER	AMOUNT OF CONCENTRATED H_2SO_4 SPECIFIC GRAVITY 1 81 ADDED	pH AFTER TREATMENT
	cc.	
1*	0.125	6.4
2	0.250	6.3
3	0.375	6.2
4	0.500	6.2
5	0.625	6.0
6	1.250	5.0
7	0.000	6.4

* All treatments were in triplicate, and, with few exceptions, all results are averages of these.

TABLE 3

Sulfur oxidation as indicated by reaction and availability of phosphate after various periods of incubation

NUMBER OF CULTURE	7 DAYS		18 DAYS		27 DAYS		37 DAYS		44 DAYS	
	pH	Available P	pH	Available P	pH	Available P	pH	Available P	pH	Available P
		per cent		*per cent*		*per cent*		*per cent*		*per cent*
1	5.1	4.5	3.8	5.0	3.8	5.2	3.4	6.4	3.2	7.5
2	5.0	4.8	3.8	5.1	3.8	5.32	3.0	5.9	3.2	8.7
3	4.8	4.6	3.6	5.1	3.6	5.48	3.4	6.3	3.2	7.4
4	5.2	4.5	3.8	5.15	3.8	5.26	3.8	...	3.8	7.4
5	5.4	4.8	4.8	5.1	4.6	4.81	3.9	5.0	4.1	5.48
6	4.6	4.3	4.6	5.0	4.6	5.12	3.6	5.1	...	...
7	6.2	4.3	4.8	5.0	4.2	5.2	3.8	5.0	3.7	6.4

NUMBER OF CULTURE	65 DAYS		86 DAYS		100 DAYS		114 DAYS	
	pH	Available P	pH	Available P	pH	Available P	pH	Available P
		per cent		*per cent*		*per cent*		*per cent*
1	3.2	17.6	3.2	19.1	3.0	24.9	2.6	31.7
2	3.2	15.9	3.2	19.0	2.8	25.1	2.8	28.4
3	3.4	16.0	3.4	18.0	3.0	24.0	3.0	26.7
4	3.8	14.6	3.8	16.7	3.8	20.1	3.8	20.4
5	3.8	14.5	3.8	15.9	3.2	20.4	3.2	20.6
6	...	...	...	...	...	...	...	...
7	3.8	15.4	4.0	16.1	3.2	21.8	3.2	21.6

to be explained. The added sulfuric acid, it might seem, reacts with the tricalcium phosphate liberating the dicalcium and monocalcium phosphates, and thereby gives these cultures a start. That the case is not so has been shown by the results presented in table 3. It seems that the acid instead of

attacking the tricalcium phosphate was absorbed or adsorbed by the so-called inert material, the soil.

What effect will the addition of sulfuric acid have on the microbial flora harboring the mixtures? No definite answer can be given and only postulates may be advanced, postulates based on the general principles of our knowledge in microbiology. It is known that different groups of organisms and species in the same group differ in their tolerance toward the reaction of the media. A detailed discussion of this question may be found in the paper of Waksman and Joffe (11). It is probable that the addition of small amounts of acid eliminated from the field undesirable competitors, and gave free range to the sulfur oxidizers. The rise in the hydrogen-ion concentration of the first three cultures seems to substantiate the advanced postulate. On the other hand, greater amounts of sulfuric acid seem not only to kill most of microbial flora, but even shock the strongest sulfur oxidizers. The sulfur-oxidizing bacteria will tolerate a reaction in sulfur-floats-soil mixtures as low as the pH 1.0, or lower. Pure cultures of a strong oxidizing bacterium reported by the writer (5) developed in a culture medium an acidity that required, for neutralization, 8.3 cc. of 0.1N NaOH per cubic centimeter of medium. These organisms were viable and upon transfer into favorable culture medium developed and functioned. The same organism when placed in a medium adjusted with sulfuric acid to a pH = 1.0 in some cases refused to grow and in other cases developed but very slowly. Lipman and Joffe (7) have shown that sulfur oxidation goes on rapidly in mixtures of 5 gm. of sulfur, 15 gm. of floats and 100 gm. of soil. The rôle of the latter in these mixtures is still obscure. The sulfur oxidation goes on rapidly. Because of the rapidity of oxidation, the possible influences in the competitive struggle of the microbial flora are obliterated. The amount of the soil is important because of its absorbing and adsorbing power. Under the conditions of the experiment reported in this paper, the addition of small amounts of acid seem to benefit sulfur oxidation.

COURSE OF CONVERSION OF INSOLUBLE PHOSPHATES INTO SOLUBLE PHOSPHATES IN SULFUR-FLOATS-SOIL MIXTURES

It has been pointed out that there are two sets of reactions involved in the process of making phosphates available by composting sulfur-floats-soil mixtures, that of sulfur oxidation and that of the action of sulfuric acid on floats. The reactions involved in the conversion of raw rock phosphate into soluble forms by means of acids belong to the type of reactions of *heterogeneous* systems. The rock phosphate minerals have no definite composition and the products formed are not always definite. In such *heterogeneous* systems the speed of the reaction is a function of a greater number of variables than in the case of a homogeneous system. According to Kazakow (b), there are factors which are common to both systems and they are:

1. Concentration of the reacting mass
2. Temperature of the reacting medium
3. Amount of contact of the reacting substances
4. Speed of diffusion of the reacting substances
5. Catalytic agents

Besides these factors we have others in a heterogeneous system where solid solution phases occur. These are:

6. Size of contact surface[3]
7. Chemical composition of the solid phase
8. Physical properties of the solid phase
9. Influence of formation of a solid phase as a result of the reaction

Factors 7 and 8 have a tremendous influence on the speed of the reaction and they are the least known, since the chemical make-up of the rock phosphate is still obscure. Kazakow (6) formulates the reactions involved in the formation of soluble phosphates as follows:

TREATMENT	RESULTS	
	Liquid phases	Solid phases
1. H_2SO_4 added in excess...	H_3PO_4, H_2SO_4, sulfates of Ca, Al, Fe	$CaSO_4 . 2H_2O$
2. Close to optimum	H_3PO_4, sulfates of Ca, Al, Fe	$CaSO_4 . 2H_2O$
3. Optimum.....	H_3PO_4, sulfates of Ca, phosphates of Al and Fe	$CaSO_4 . 2H_2O$
4. Not enough acid.....	H_3PO_4, sulfates of Ca, phosphates of Ca, Al and Fe	$CaSO_4 . 2H_2O$ and part of undissolved phosphate

In the acid phosphate, or super-phosphate industry the idea is to obtain monocalcium phosphate and for convenience the reaction is represented as follows:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2\,CaSO_4 . 2H_2O.$$

As it may be deduced from the scheme presented by Kazakow enough acid has to be used to accomplish this reaction; the practice is to use acid containing about 30 to 38 per cent of water (chamber acid of 50° B), since much water is necessary for the gypsum formation.

In the case of the sulfur-floats-soil mixtures, the amount of sulfuric acid formed at any moment is small and in the presence of the large amounts of tricalcium phosphate no accumulation of acid is possible; the reactions are slowly approaching equilibrium and coming to completion. The transition

[3] The size of the particles of the rock in the manufacture of acid phosphate has a tremendous influence. Theoretically, all other conditions being equal, the speed of solution of a solid in a liquid is proportional to the contact surface, and in spherical bodies (as we suppose in fine floats) the surface is proportional to the square of the radius. Particles with a radius of 0.1 mm. will dissolve twenty-five times as fast as particles with a 0.5 mm. radius.

stages are drawn out, e.g., the conversion from the tertiary to the primary phosphate is slow, since there is never an excess or a rapid formation of sulfuric acid. In a liquid medium where pure cultures of the sulfur-oxidizing organism were used (5) the steps involved in the transformation of the tertiary to the primary phosphates may easily be followed. The conditions in the culture medium are ideal for sulfur oxidation and the transition stages are short, e.g., the secondary phosphates quickly come to equilibrium with the tertiary

TABLE 4

Sulfur oxidation in a liquid medium

AGE OF CULTURE	NUMBER OF CULTURE	pH	SOLUBLE PHOSPHORUS PER 100 CC OF MEDIUM*	AGE OF CULTURE	NUMBER OF CULTURE	pH	SOLUBLE PHOSPHORUS PER 100 CC. OF MEDIUM*
days			*mgm.*	*days*			*mgm.*
1	1	5.4	45.94	9	12	2.7	87.44
	2	5 4	45.39		14	2.7	95.16
	3	5.4	45.39		15	2.6	93.56
2	4	5 4	42.46	11	18	2.8	84 68
	5	5.4	42.75		19	2.6	101.25
3	6	5.3		13	20	2.3	183.51
	7	5 3	47.20		21	2.3	189.08
5	8	5.2	49 15	15	22	2.3	200.22
	9	4.0	60 80		23	2.3	206.70

* The total amount of phosphorus in 100 cc. of medium was 217.8 mgm.

phosphate and allow a rapid formation of the primary phosphate. The data recorded in table 4 demonstrate this point. The medium used was of the following composition:

	gm.
K_2HPO_4	1.00
$MgSO_4$	0.50
KCl	0.50
$FeSO_4$	0.01
$(NH_4)_2SO_4$	2.00
Sulfur	10.00
$Ca_3(PO_4)_2$	10 00

The medium was distributed in 250-cc. Erlenmeyer flasks and sterilized in flowing steam for ½ hour each day for 3 consecutive days. A series of flasks was inoculated and incubated at 27°C. Every day two or three flasks were taken out and analyzed for the hydrogen-ion concentration and soluble phosphates.

The interesting point of these data is that the crucial reaction for the conversion of the insoluble phosphates into soluble phosphates is that obtaining at

a hydrogen-ion concentration pH 2.7. It was apparent that at this point the primary phosphate was formed, which reacted with the tertiary, formed secondary and, in combination with the sulfuric acid constantly being formed in the cultures, completed the reaction. The transformation of the phosphates beginning at the pH = 2.7 went on very rapidly and within 4 days almost all of the phosphates have been made soluble. It is interesting to point out that the hydrogen-ion concentration of the chemically pure monobasic calcium phosphate and that of commercial acid phosphate is 2.6–2.7. When we examine the cultures of the sulfur-floats-soil mixtures in the aeration work and investigate the course of the reaction we also find that the reaction goes down to a pH 2.8–2.6 and remains at this point for a long time, contrary to what is happening in the liquid cultures. It seems that the amount of the monobasic salt formed is very small and it takes time for the reaction to come to completion. The driving force of the reaction is the sulfuric acid and the speed of its production by the microörganisms thus determines the velocity of the reaction.

It is known that fluorides are present in almost all phosphate rock, usually as calcium fluoride. The latter reacts with sulfuric acid, giving hydrogen fluoride and calcium sulfate as shown in the equations:

$$CaF_2 + H_2SO_4 = 2\ HF + CaSO_4$$

The hydrogen fluoride is a strong reagent and reacts with the silicates of the phosphate minerals forming silicon tetrafluoride:

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

The gaseous silicon tetrafluoride is decomposed by water forming hydrofluosilicic acid and precipitating pure silica:

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$

In the process of making acid phosphate most of the silicon tetrafluoride escapes and to a certain extent is beneficial to the process, since it makes the mixture more porous. The presence of this gas could be detected by its well known penetrating odor in the sulfur-floats-soil mixtures, especially when the sulfur-oxidizing organisms were active. The effect of this gas on the pure cultures of the sulfur-oxidizing microörganisms has not yet been studied. In mixtures with only 15 per cent of rock phosphate, 100 per cent conversion of the insoluble phosphates into soluble phosphates has been accomplished in 7 and 8 weeks, and in such cases, the odor of the silicon tetrafluoride was at times very strong.

This seems to indicate that the gas has no deleterious effect on the organisms. Still a more detailed study with the pure organisms is to be taken up, before any definite statement can be made. The other constituents of the minerals of rock phosphate undoubtedly play their part. With all the handicaps and

unknowns in the process, in the case of the aeration study as shown in table 1, 50 per cent of the phosphates has been made available.

One point is to be remembered in making analysis for the soluble phosphates: the total phosphates must be determined every time, since the percentage of the total will vary in the sample, for the oxidation of the sulfur, as shown in the earlier part of this paper, increases the weight of the mixture. It will therefore decrease the percentage of total phosphorus while the soluble phosphates will increase proportionally. This point has been overlooked in the earlier work at the New Jersey Agricultural Experiment Station as well as by workers of other stations.

The problem of making acid phosphate by the Lipman process of mixing rock phosphate, sulfur and soil is therefore chiefly a problem of providing ideal conditions for the sulfur-oxidizing bacteria. The different environmental conditions, variation of treatment, effect of temperature, inoculation and many other factors will be taken up in another paper. It will be shown that making phosphates available by the Lipman process has tremendous possibilities. In certain cropping systems this process will replace acid phosphate.

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THE ORGANIC PHOSPHORUS CONTENT OF SOME IOWA SOILS

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The form in which phosphorus occurs, as well as its function in soils has been the subject of much study. Many years ago it was suggested that part of the phosphorus in soils occurs in an organic form, but some investigators doubted the occurrence of sufficient amounts to be of any significance. Various methods of determining the mineral phosphorus compounds in soil have been suggested, but it is only comparatively recently that a method has been developed which serves to distinguish between organic and inorganic phosphorus, and to show that there is an appreciable amount of the former in most soils. Potter and Benton (6) first attempted to determine organic phosphorus in soil and they devised a method which proved quite satisfactory. Schollenberger (7) studied the problem later and modified the method slightly. His conclusions agreed with those of Potter and Benton, however, in showing that there is a rather large amount of soil phosphorus in the organic form. Very little work has been done as yet to show the relationship of organic phosphorus to other constituents of the soil and to the fertility of particular soil types. It would be very desirable to know the relation organic phosphorus bears to fertility. Is it more or less available to plants than inorganic phosphorus? Does organic phosphorus revert to the inorganic form and how rapidly? These, and many other questions remain to be answered when more is known about the organic phosphorus content of soils.

A review of the literature shows that as early as 1844 Mulder (1) noted the presence of phosphorus in organic soil material.

Schmoeger (2) studied the effect of igniting soil and of heating with water under pressure, and concluded that the increased solubility of phosphorus in hydrochloric acid after ignition was due to the destruction of insoluble organic phosphorus compounds. He concluded that the phosphorus was in the form of nuclein or similar compounds.

Hopkins and Pettit (3) noted that certain soils showed a uniform mineral composition in surface, subsurface, and subsoil, and suggested that the difference in phosphorus in surface and subsoil might be due to organic phosphorus. They suggested a method for calculating organic phosphorus.

[1] The author wishes to acknowledge his indebtedness to Dr. P. E. Brown for suggestions and criticisms in preparing the manuscript.

Stewart (4) discussed the solubility of soil phosphorus in hydrochloric acid and ammonia and concluded that the greater part at least of the ammonia-soluble phosphorus is organic.

Fraps (5) showed that inorganic phosphates were soluble in ammonia after ignition and extraction with hydrochloric acid. He concluded that no method previously advocated would distinguish between organic and inorganic phosphorus in ammonia extracts.

Potter and Beuton (6) originated a method for distinguishing between organic and inorganic phosphorus in ammonia extracts.

Schollenberger (7) developed further the method of Potter and Benton and he discussed the relationships between organic phosphorus and other constituents. He concluded that organic phosphorus and nitrogen exist in the same ratio at different depths.

EXPERIMENTAL

The object of this paper is to describe some preliminary experiments in a study of the organic phosphorus content of several Iowa soils.

The four soils used were selected so as to give as wide a range of conditions as possible and are described below.[2]

No. 1. Wabash silty clay loam. "A dark brown to black silty clay loam to a depth of 18 inches, becoming somewhat lighter in color at that point. A dark brown to lighter brown silty clay loam to silty clay or clay to a depth of 36 inches. The soil is level and often poorly drained." The organic matter content is very high. Both surface and subsoil are low in lime. This soil when properly drained and worked is capable of very high productivity. This soil in its native condition may, in spite of its poor drainage and low bacterial activity, be said to possess high latent fertility.

No. 2. Clinton silt loam. "The surface soil is a light brown to grayish-brown silt loam. This extends to a depth of 8 to 12 inches at which point it grades into a layer of yellowish-brown or yellowish-gray silty clay mottled with yellowish-brown. This intermediate layer is usually 4 to 8 inches in depth and changes abruptly into a yellowish-gray silty clay mottled with yellowish-brown and rusty brown. This subsoil is very plastic when wet and compact and hard when dry." The drainage is good, but the soil washes badly. The organic content of the soil is low. The phosphorus content is comparatively low and the soil reaction is acid.

No. 3. Hancock silty clay. "The surface soil is only 4 to 6 inches in depth, and the subsoil extends to 12 to 15 inches giving way below to a gray and brown mottled or drab plastic clay which extends to 3 feet or more." The soil is rather high in total phosphorus and low in organic matter.

No. 4. Jackson silt loam. "The surface soil is a light-brown, smooth, silt loam to a depth of 8 to 12 inches and passes into a yellowish-brown silty clay loam to silty clay. The subsoil is rather compact." The application of lime where the soil is acid and of phosphorus and organic matter gives good results. This particular soil was selected because of its low phosphorus and organic carbon content and because of its acidity and low fertility.

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[2] Quotations are taken from Soil Survey Reports of Iowa: Soil No. 1, Wright County Soils (in press); Soil No. 2, Johnson County Soils (in press); Soil No. 3, Pottawattamie County Soils; Soil Survey Report No. 2; Soil No. 4, Henry County Soils; Soil Survey Report No. 15.

No. 1. High organic carbon, phosphorus, and nitrogen, high latent fertility.
No. 2. Low nitrogen and organic carbon, relatively high total phosphorus.
No. 3. High total phosphorus and low organic carbon, high nitrogen.
No. 4. Low phosphorus, carbon and nitrogen, low fertility.

The analytical data given in table 1 with the exception of those giving organic phosphorus are taken from the analyses made in connection with the work of the Iowa Soil Survey.[3] The organic phosphorus results were obtained by the method developed by Schollenberger with some slight modifications. This method involves the preliminary extraction of the soil with 1 per cent HCl followed by the extraction of the phosphorus by eight hours shaking with 4 per cent ammonia. After the extraction with HCl, the soil was washed free

TABLE 1

Analyses of soils

SOIL STRATUM	ORGANIC CARBON	NITROGEN	PHOSPHORUS	ORGANIC PHOSPHORUS
	lbs. per acre	*lbs. per acre*	*lbs. per acre*	*lbs. per acre*
Soil 1:				
Surface	129,354	9,500	1,563	393.46
Subsurface	178,542	9,760	2,398	482.40
Subsoil	116,298	6,180	2,304	690.36
Soil 2:				
Surface	20,256	1,500	1,428	72.22
Subsurface	12,448	1,000	2,560	
Subsoil	18,509	1,320	3,072	233.82
Soil 3:				
Surface	52,428	4,380	1,900	289.40
Subsurface	73,016	6,800	3,120	422.80
Subsoil	63,834	6,600	4,260	623.40
Soil 4:				
Surface	26,880	2,376	830	289.40
Subsurface	21,960	2,123	1,278	267.40
Subsoil	23,280	2,433	2,124	345.18

from chlorides, dried and ground to pass thru a 100-mesh sieve. 75 gm. were shaken with 750 cc. of 4 per cent ammonia. The soil suspension was set aside to settle then filtered through porcelain filters under 45 pounds pressure. This method of separation is open to some objection because it has been found that part of the organic matter does not pass through the filter. However, there was no difficulty experienced in the filtration. Soil no. 1 with the highest organic matter content filtered more slowly, but in every sample all but a few cubic centimeters filtered through. If there were any great discrepancy in results due to the filtration it should show up in soil no. 1. Here, however,

[3] The soil survey of Iowa is carried out by the Soils Section of the Iowa Agricultural Experiment Station in cooperation with the Bureau of Soils of the United States Department of Agriculture.

there was found a high percentage of organic phosphorus. Fraps (8) found with pure humic acid as much as 10 per cent loss in filtration. Schollenberger in comparing total phosphorus in an original ammonia soil extract with one filtered through unglazed porcelain found 6.6 per cent loss. Granting a loss of 10 per cent, the differences in percentages of organic phosphorus in the soil types used was so great that the value of the comparisons is not lost. In following up this preliminary work, however, a method of separation will be used which will eliminate this factor of loss.

Total phosphorus was determined from a 100 cc. portion of the filtrate. Inorganic phosphorus was determined from an equal aliquot. Organic

TABLE 2

Ratios of various constituents

SOIL STRATUM	NITROGEN-CARBON RATIO	ORGANIC PHOSPHORUS-TOTAL PHOSPHORUS RATIO	ORGANIC PHOSPHORUS-ORGANIC CARBON RATIO	ORGANIC PHOSPHORUS-NITROGEN RATIO
Soil 1:				
Surface	1–13.6	1– 3.98	1–328.7	1–24.1
Subsurface	1–18.3	1– 4.97	1–370.1	1–20.2
Subsoil	1–18.6	1– 3.34	1–168.4	1– 8.9
Soil 2:				
Surface	1–13.5	1–19.84	1–280.4	1–20.7
Subsurface	1–12.4			
Subsoil	1–14.0	1–13.15	1– 79.2	1– 5.6
Soil 3:				
Surface	1–11.9	1– 6.57	1–181.1	1–15.1
Subsurface	1–10.7	1– 7.40	1–172.6	1–16.0
Subsoil	1– 9.6	1– 6.84	1–102.3	1–10.5
Soil 4:				
Surface	1–11.3	1– 2.87	1– 92.8	1– 8.2
Subsurface	1–10.3	1– 4.80	1– 82.1	1– 7.9
Subsoil	1– 9.5	1– 6.17	1– 67.7	1– 7.0

phosphorus was obtained by taking the difference. All determinations were run in duplicate. It will be noted that in some cases rather large proportions of the total phosphorus were in organic form.

DISCUSSION OF RESULTS

Table 2 gives the calculations of the nitrogen-carbon, organic phosphorus-total phosphorus, organic phosphorus-organic carbon, and organic phosphorus-nitrogen ratios. By examining this table it may be seen that the nitrogen-carbon ratio is wider in soil no. 1 than in any of the other soils. This is as might be expected since soil no. 1 contains much more organic matter than any of the other soils. There has been less cropping on this soil than on the average upland soils of this section, drainage is poor and aeration deficient; hence organic matter has accumulated. Soil no. 4 shows the narrowest ratio;

and although it is very little different from no. 3, more decomposition and greater loss of easily decomposed organic matter has evidently occurred in this type.

When the ratio of organic phosphorus to total phosphorus is observed some interesting comparisons will be noted. For instance, the soil having the highest latent fertility (soil no. 1) and the soil having the lowest latent fertility (soil no. 4), show the highest ratios of organic phosphorus to total phosphorus. However, it is not fair to compare these two soils from the phosphorus standpoint alone since soil no. 1 is well supplied with nitrogen and has nearly twice as much total phosphorus. The significant part of the comparison is that a soil like no. 4 which is comparatively low in fertility and with so low a total phosphorus content should have 34 per cent of its phosphorus in organic form. This seems to indicate that organic phosphorus is perhaps less available than inorganic and remains in organic form rather tenaciously. In soil no. 4 if organic phosphorus were readily changed to inorganic it would hardly be expected that so large a percentage of organic phosphorus would be found. Following this line of reasoning it would be expected that soil no. 2 with only 5 per cent organic phosphorus would show a greater response to nitrogen than to phosphorus, since it has only 1500 pounds of nitrogen and has a comparatively high amount (1428 pounds) of total phosphorus of which only 5 per cent is organic.

Table 2 shows that with the exception of soil no. 4 the ratio of organic to total phosphorus is fairly constant at all depths. Soil no. 4 has evidently lost more of its inorganic phosphorus.

The organic phosphorus-nitrogen ratio shows a very striking contrast to the organic phosphorus-total phosphorus ratio. There is a wider ratio in the surface soils in all cases than in the subsoils in the former. This indicates that the nitrogen accumulated at the surface and made soluble has been leached out more rapidly than has the organic phosphorus. This of course is not surprising.

It may readily be seen from table 2 that the ratios of organic phosphorus to organic carbon are so different that no one ratio will serve for calculating organic phosphorus from organic carbon in different soil types. There is a range in ratios in surface soils from 1 to 328.7 in soil 1, to 1 to 92.8 in soil 4. However, if a large number of determinations had been made on each type it is possible, though not probable, that a more satisfactory and uniform ratio might have been secured.

Table 3 shows the amounts in all soils at different depths based on 2,000,000 pounds for surface, subsurface and subsoil. It is interesting to observe that organic phosphorus is rather uniform in subsurface and subsoil in all cases. Unfortunately the subsurface determination of soil no. 2 was lost.

The only explanation which can be suggested for this is that the organic phosphorus in the soil, or the phosphorus called organic, seems to remain as such and is rather uniformly distributed throughout the soil with the exception

of the surface where the amount has been increased by decaying plant residues.

No attempt has been made to draw any conclusions from these few analyses. This paper is merely a preliminary report on the problem. The results are interesting and indicative of the need of further study of organic phosphorus, but they will not permit of definite conclusions.

TABLE 3

Organic phosphorus in soil on basis of 2,000,000 pounds of soil for surface, for subsurface, and for subsoil

SOIL STRATUM	ORGANIC PHOSPHORUS
	lbs.
Soil 1:	
Surface	393.46
Subsurface	241.20
Subsoil	230.12
Soil 2:	
Surface	72.22
Subsurface	
Subsoil	77.94
Soil 3:	
Surface	289.40
Subsurface	211.40
Subsoil	211.70
Soil 4:	
Surface	289.40
Subsurface	133.70
Subsoil	115.09

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SOME EXPERIMENTS ON RECLAMATION OF INFERTILE ALKALI SOILS BY MEANS OF GYPSUM AND OTHER TREATMENTS

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The experiments reported here were made during the year 1920 in the hope of finding out as quickly as possible what might be accomplished to restore fertility by simple treatments to the alkali soils of the University Farm at Kearney Vineyard near Fresno, California. Some of these soils had once been capable of producing excellent crops, but have now become so filled with alkali that little of value will grow on them. The immediate object of these experiments was to determine what kind of treatments should be tried in the fields to restore fertility to these alkali soils.

During the years 1914–18 the Experiment Station had endeavored to reclaim an area of 160 acres of this land known as the Experimental Drainage Tract. A system of tile drains was installed, the land was flooded, and thus a large amount of saline and alkaline matter was removed in the drainage. Yet the land was not permanently reclaimed. Much of it remained bare, or covered only with alkali weeds.

At a conference at the University in August, 1919 it was decided to make a detailed survey to determine the extent and nature of the alkali. After the tract had been mapped, a ton or more of soil from each of five localities representing the chief variations in alkalinity was brought to the laboratory for experimental study. The soils were air-dried, screened and thoroughly mixed, then stored in closed bins in the house.

THE CHARACTER OF THE SOILS

There is considerable variation in the physical character of these soils, but in general they are classed as Madera fine sandy loam. No. 15 is a fertile, non-alkaline soil taken from the grove of ornamental trees. It was used as a check or standard to show what might be expected from a similar soil which contained no alkali.

In respect to alkali these soils beginning with the worst, may be described as follows:

No. 16 is a strongly alkaline and saline soil from area 118 of the Experimental Drainage Tract, section 6. It is devoid of any vegetation.

No. 17 was originally a similar soil from area 58 of the Experimental Drainage Tract but it had been leached in the field and later cropped. Leaching had removed the alkali and

salts so that it contains less than one-fourth as much as soil 16, but it is still very toxic and unable to support vegetation.

No. 18 is a highly saline but not alkaline soil from the olive orchard. It is too saline to permit much growth of crops.

No. 19 is a moderately alkaline and saline soil from area 200 on North Monarch Vineyard. It supports a moderate growth of barley.

No. 20 is a similar soil from the same locality, but is more alkaline, and highly saline. It is very infertile.

The general composition and qualities of these soils are indicated in tables 1 and 2. They show that the soils are similar in ultimate composition. The chief variations are in Na, Cl, SO_4 and CO_3, which are the characteristic constituents of alkali soils. These differences are more apparent in the water extracts, especially in those made with carbon-dioxide-free water.

THE VARIOUS TREATMENTS

Originally it was intended to treat the soils only with gypsum in varying amounts. Later it was seen that gypsum was not effecting the restoration of these soils to productiveness. Accordingly, as opportunity offered, various other procedures were tried, but only to a very limited extent on account of lack of time and facilities. The leaching of soil 18 should be regarded as a separate experiment, as this soil was not alkaline.

The soils varied greatly in alkalinity and in salinity, hence all were not treated alike. Soils 16 and 17 were so highly alkaline that it was hardly expected to restore fertility in them by gypsum alone, so only one pot of each treatment was prepared. It was hoped that some amount of gypsum would improve soils 19 and 20 so that they would produce a crop, hence each treatment was tried in seven pots, in order to obtain somewhat average or representative results.

The gypsum treatments of soils 16 and 17 were made by G. R. Stewart about three months previous to the time the treatments on soils 18, 19 and 20 were started. The treatments for the latter soils were decided upon at a conference between Professors J. S. Burd and D. R. Hoagland and the writer.

The gypsum, or other added material, was mixed with the dry soil, then the mixture was placed in 5-gallon earthenware jars and watered. After a few days barley was planted in the jars.

Soils 16 and 17 were treated alike with gypsum ($CaSO_4 2H_2O$) in amounts from 500 to 80,000 pounds per acre.

Soil 18, saline not alkaline, was leached only.

Soils 19 and 20 were treated with gypsum in amounts of 3000 to 64000 pounds per acre.

Organic treatments

One jar each of soils 16, 17, 19, 20 was mixed with 1 per cent of its weight in rotted manure; one jar of each with 1 per cent in alfalfa meal; and one of each with 2 per cent in lawn (blue-grass) clippings. These were planted and cared for like the gypsum treatments.

The leaching treatments

Soil 18 was the only one extensively treated by leachings.

This very saline, but not alkaline soil required only leaching to remove the excess of salts in order to restore fertility. Two qualities of water were used; first, the ordinary tap water.

TABLE 1

Composition of the water extracts of alkali soils

Ratio of soil to water—1:5

SOIL CONSTITUENTS	QUANTITIES FOUND IN SAMPLES EXPRESSED AS PARTS PER MILLION IN DRY SOIL				
	No. 16	No. 17	No. 18	No. 19	No. 20
Extract made with ordinary distilled water, filtered on Pasteur filter					
	p. p. m.	*p. p. m.*	*p. p. m.*	*p. p. m.*	*p. p. m.*
Total solids.	26,695	6,128	8,173	2,296	4,934
Ca.	61	25	450	31	26
Mg.	7	8	169	8	9
Na.	9,682	2,046	1,545	707	1,670
K.			116		
SO_4.	1,807	822	677	509	550
NO_3.			1,624	112	329
CO_3.	2,457	302	0	0	0
HCO_3.	4,995	983	259	499	504
Cl.	7,988	1,663	1,444	611	1,681
Extract made with distilled water free of CO_2, filtered on paper					
CO_3.	3,300	600	0	48	120
HCO_3.	3,050	610	61	238	183
Cl.	7,600	1,850	1,275	635	1,825

TABLE 2

*Composition of acid extracts of alkali soils**

SOIL CONSTITUENTS	QUANTITIES FOUND IN SAMPLES EXPRESSED AS PERCENTAGES OF DRY SOIL.				
	No. 16	No. 17	No. 18	No. 19	No. 20
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Insoluble residues.	88.43	89.78	77.98	88.54	88.80
Soluble silica.	0.42	0.46	0.50	0.51	0.45
Fe.	1.97	2.05	3.42	2.31	2.01
Al.	1.24	1.21	4.31	1.64	1.69
Ca.	0.91	0.80	0.90	0.81	1.04
Mg.	0.45	0.45	0.51	0.44	0.41
Na.	1.13	0.41	0.29	0.22	0.18
K.	0.52	0.57	1.34	0.65	0.35
SO_4.	0.20	0.08	0.15	0.06	0.04
PO_4.	0.06	0.05	0.05	0.04	0.09
Cl in water extract.	0.80	0.17	0.14	0.06	0.17
Organic, loss, water, etc.	3.33	3.79	10.18	4.64	4.62
Total CO_2 by evolution.	0.54	0.18	0.07	0.07	0.12
Acid Equivalent = $\%H_2SO_4$ required to neutralize.	0.98	0.31	0.015	0.088	0.157
Hydrogen Ion Concentration of moist soil (pH).	9+	9+	7.0	8.2	8.6

*Extract made according to method of Association of Official Agricultural Chemists, HCl specific gravity 1.115, 10 hours in steam bath.

Calcium and magnesium bicarbonates constitute the chief soluble ingredients of this water. It was considerably superior to the synthetic water no. 1 in facility of leaching, and left the soil in better physical condition. Barley seemed to do better on the soil leached with tap water.

Sodium carbonate (20 p.p.m.) is the characteristic constituent of synthetic water no. 1 used to leach the duplicate lot of soil 18. This water tended to puddle the soil and percolated much more slowly than the tap water. Long use of such a water for irrigation might be expected to produce an alkali soil.

It is thought that the tap water was superior on account of its content of calcium which maintained flocculation of the soil.

The procedure employed was as follows:

Fifty pounds of soil was placed on muslin cloth in a large galvanized filter 2½ feet in diameter. The soil made a layer 1½ to 2 inches thick. A nearly equal volume of water, 8 liters, was added and allowed to run through. Then 8 liters more were added; after it ran through, 8 liters more. After this, suction was applied for several hours until no more water was removed. Then the soil was taken out, spread on paper and left in a warm room until dry. Later it was pulverized and mixed and returned to the jars.

A few leachings were made on soil 16. One lot leached with distilled water containing 0.1 per cent gypsum was placed in jar 131. One lot was leached in a similar manner with synthetic water no. 1 containing 0.1 per cent gypsum. It was in two portions, one placed in jar 133 remained quite alkaline and saline. Enough sulfuric acid to neutralize the soil was added to the last leaching water applied to the other. Still retaining much saline matter, it was placed in jar 132. Barley germinated well in these soils, but died without making much growth. The physical condition of these soils was very bad. They were badly puddled, and not easily penetrated by water. This effect was generally observed after leaching a very alkaline soil.

Leaching in Glass Tubes

Although this was a separate experiment it is of interest in this connection to mention the results obtained.

The soils were placed in glass tubes about 1 inch in diameter, 4 to 5 feet long. The soil columns were about 4 feet long. They were leached with synthetic water no. 1 and no. 2. The tubes were too narrow and several of them broke so that results were unsatisfactory.

In general, the more saline water no. 2 percolated more rapidly than the alkaline water no. 1. After the larger proportions of the salts had been removed from soils 16 and 17, percolation very nearly ceased. On soils 19 and 20 percolation became very slow toward the last, but finally nearly all the salinity and most of the alkalinity was removed. These soils are much more easily leached than 16 and 17.

RESULTS OF SOIL TREATMENT

The crop of barley

Barley was the crop selected to indicate the effect of the treatments. The soils were placed in 5-gallon stone-ware jars, each holding about 50 pounds of soil. Seed was planted in January. During the time the crop was growing, the jars stood in an open shed with a glass roof, so that the soils were exposed to ordinary weather conditions except that rain was excluded. The moisture content was maintained near the optimum (15 to 18 per cent— by frequent additions of distilled water. After the crop had matured and dried, it was harvested and the weights of heads and of stalks recorded. Seven jars of the fertile soil 15 were used for checks and cropped in the same manner.

The crop produced is taken as somewhat indicative of the degree of improvement in the various soils consequent on the treatments applied.

Except in the case of one treatment only none of the seeds planted in soil 16 germinated. On some of the leached soils there was fair germination but very little growth. Soil 17 permitted some germination, but little crop. Soils 18 and 19 produced considerable crop as shown in table 3. Soil 20 allowed some germination, but the plants soon ceased to grow.

TABLE 3

Relative yields of barley on treated alkali soils

SOIL NUMBER	TREATMENT	YIELD OF HEADS AND STALKS		YIELD OF HEADS			
		Total weight	Comparison with "check"	Total weight	Comparison with "check"	Number of heads	Comparison with "check"
		gm.	*per cent*	*gm.*	*per cent*	*gm.*	*per cent*
15	None (check).....	37.0	100	19.5	100	12.3	100
16	Gypsum, all amounts,....	*		*		*	
17	500 lbs. gypsum.....	3.0	8	0.5	3	2.0	16
17	32,000 lbs. gypsum..	11.5	31	3.5	18	5.0	40
17	80,000 lbs. gypsum	8.0	22	2.5	13	5.0	40
18	None.....	4.3	12	1.3	7	4.3	35
18	Leached, tap water.....	39.4	106	17.3	89	14.7	119
18	Leached, synthetic water.	33.6	91	16.9	87	13.3	108
19	None.....	7.2	19	3.9	20	6.0	48
19	2000 lbs. gypsum.....	9.1	25	5.1	26	7.9	64
19	8000 lbs. gypsum.....	12.0	32	6.9	35	10.6	86
19	16,000 lbs. gypsum.....	13.1	35	7.6	38	11.9	97
19	64,000 lbs. gypsum.....	16.1	44	9.5	48	13.0	106
20	Gypsum, all amounts....	†		†		†	

* No germination.

† Some germination, but no crop.

When the toxicity is sufficiently overcome by gypsum and leaching to permit a fair growth of crop, it appears that the plants bear an undue number and weight of heads in proportion to total weight. This may be due to the endeavor of the plant to reproduce itself under adverse conditions of nutrition.

Changes in alkalinity

Four or five weeks after the barley had been planted, when the effect of the alkali on the plants was evident, samples of soil were taken from both top and bottom of jars representing nearly all the different treatments.

TABLE 4

Effects of treatments on soil

SOIL	TREATMENT	pH VALUE OF SOIL EXTRACT	H_2SO_4 REQUIRED TO NEUTRALIZE 1-10 EXTRACT BY		H_2SO_4 REQUIRED TO NEUTRALIZE, MUD SUSPENSION	CHLORINE
			Phenolphthalein	Methyl orange		
	per acre		*per cent**	*per cent**	*per cent**	*per cent**
No. 15						
Top	None	6	0.000	0.014	0.000	0.006
Bottom	None	6	0.000	0.010	0.000	0.010
No. 16						
Original	None	9+	0.255	0.745	0.98	0.78
Top	1000 lbs. gypsum	9+	0.274	0.676		0.68
Bottom		9+	0.290	0.764		0.68
Top	8000 lbs. gypsum	9+	0.235	0.598		0.72
Bottom		8+	0.290	0.715		0.73
Top	80,000 lbs. gypsum	9+	0.050	0.120		0.57
Bottom		9+	0.070	0.137		0.66
Top	Alfalfa	9+	0.220	0.510		0.46
Bottom		9+	0.372	0.884		0.92
Whole jar	Leached and neutralized	6.5	0.000	0.016	0.010	0.01
Whole jar	Leached with gypsum	9+	0.027	0.059	0.137	0.00
No. 17						
Original	None	9+	0.059	0.176	0.320	0.15
Top	1000 lbs. gypsum	7.4	0.001	0.031		0.012
Bottom		8.8	0.012	0.057		0.350
Top	8000 lbs. gypsum	9+	0.023	0.074		0.076
Bottom		9+	0.015	0.104		0.224
Top	80,000 lbs. gypsum	8.5	0.008	0.033		0.050
Bottom		9.0	0.029	0.059		0.276
Whole jar	Manure, 10 tons	9+	0.039	0.127		0.03
Whole jar	Grass clippings, 20 tons	9+	0.055	0.116		0.08
Top	Alfalfa	9+	0.015	0.113		0.02
Bottom		9+	0.059	0.204		0.26
No. 18						
Original	None	7	0.000	0.016	0.015	0.134
Top	None	6.5	0.000	0.016		0.094
Bottom		6.5	0.000	0.016		0.180
Top	Leached with tap water	7.2	0.000	0.037		0.004
Bottom		6.8	0.000	0.026		0.012
Top	Leached with synthetic water no. 1	6.8	0.000	0.030		0.012
Bottom		7.2	0.000	0.034		0.006

* Per cent of the dry soil.

TABLE 4—*Concluded*

SOIL	TREATMENT	pH OF SOIL EXTRACT	H_2SO_4 REQUIRED TO NEUTRALIZE 1-10 EXTRACT BY		H_2SO_4 REQUIRED TO NEUTRALIZE, MUD SUSPENSION	CHLORINE
			Phenolphthalein	Methyl orange		
	per acre		*per cent**	*per cent**	*per cent**	*per cent**
No. 19						
Original	None	8.2	0.008	0.048	0.088	0.076
Top	None	8.8	0.010	0.051		0.020
Bottom		7.2	0.004	0.043		0.114
Top	2,000 lbs. gypsum	8.8	0.006	0.054		0.110
Bottom		7.2	0.000	0.025		0.156
Top	8,000 lbs. gypsum	6.8	0.000	0.029		0.020
Bottom		6.8	0.000	0.019		0.140
Top	16,000 lbs. gypsum	6.8	0.000	0.019		0.020
Bottom		6.8	0.000	0.019		0.100
Top	64,000 lbs. gypsum	6.6	0.000	0.019		0.030
Bottom		6.6	0.000	0.019		0.066
Top	Alfalfa	8.5	0.016	0.065	0.049	0.008
Bottom		8.5	0.008	0.069	0.049	0.170
No. 20						
Original	None	8.6	0.040	0.140	0.157	0.182
Top	None	8.8	0.020	0.064	0.074	0.160
Bottom		8.8	0.016	0.060	0.074	0.220
Top	8000 lbs. gypsum	7.2	0.002	0.036	0.037	0.220
Bottom		7.2	0.004	0.036	0.049	0.220
Top	16,000 lbs. gypsum	7.2	0.000	0.028	0.049	0.170
Bottom		7.8	0.000	0.028	0.025	0.280
Top	32,000 gypsum	6.8	0.000	0.024	0.037	0.124
Bottom		6.8	0.000	0.024	0.049	0.210
Top	64,000 lbs. gypsum	6.8	0.000	0.014	0.049	0.110
Bottom		6.8	0.000	0.026	0.049	0.220
Top	Alfalfa	8.8	0.030	0.090	0.074	0.110
Bottom		8.8	0.016	0.075	0.123	0.276

To determine the alkalinity of the soil two methods were used. In the first method, 1 to 10 water extract (CO_2-free water) was titrated with acid, with phenolphthalein and methyl orange as indicators; then Cl was determined by titration with $AgNO_3$ and chromate indicator. In the second method a suspension, or mud, containing 2 parts of soil to 1 part of water was titrated with 0.1 *N* H_2SO_4, the indicator being bromcresol purple on a white porcelain plate. Similar tests on the original soil are given for comparison. These data are shown in Table 4.

In general the table shows that gypsum reduced the total alkalinity and lowered the hydrogen-ion concentration somewhat in proportion to the amount added to the soil. In some of the mixtures there was much more gypsum than necessary to react with all the sodium carbonate in the soil. Also it is probable

that a large part of the gypsum in the higher applications did not react with the soda on account of lack of time and of sufficient water to dissolve the gypsum. Presence of calcium and sulfate in quantity, in the water extracts from the higher treatments of soils 17, 19 and 20, indicates that the gypsum had never been dissolved after being mixed with the soil. Only the highest application on soil 16 contained enough gypsum to neutralize all the soda in this soil.

The data also indicate that the soluble salts were largely removed from the top layers of soil in the jars and concentrated in the bottom during the first month after barley was planted. This undoubtedly enabled the grain to make a much better early growth than if such translocation had not taken place. It is probable that later in the period these salts migrated back toward the tops of the jars. The table also shows that the top soil in some jars had a higher hydrogen-ion concentration than the bottom. This seems to be a common effect of washing salts from an alkaline saline soil, and perhaps also from a non-alkaline soil.

The reaction between gypsum and sodium carbonate

There is usually a small amount of calcium in the water extract of most alkali soils, due to the solvent effect of sodium salts on calcium carbonate and also to replacement of calcium by sodium. But so long as the soil contains sodium carbonate enough to give it a hydrogen-ion concentration of pH-8.5 or higher, no considerable amount of calcium will be found in the water extract of the soil. This fact, together with the fact that gypsum is soluble in water only to the extent of about 0.25 per cent, sets a rather definite limit to the amount of alkali which can be neutralized by addition of gypsum to the soil without removal of the products of the reaction.

It might be thought that an excess of gypsum added to such a soil would gradually dissolve, as the reaction proceeded, so that if enough gypsum were present all of the sodium carbonate would be finally changed to sodium sulfate. But the tendency to reversal of this reaction in the presence of considerable amounts of sodium salts, is so great that it becomes impossible to neutralize large amounts of sodium carbonate in soil by gypsum, without leaching to remove the sodium sulfate. Examination of table 4 brings this out. Soils 16 and 17 did not become neutral by the addition of any amount of gypsum, though some of the applications were more than enough to combine with all the sodium carbonate present. The concentration of sodium salts was too great. On the contrary, soils 19 and 20 lost their alkalinity when treated with sufficient gypsum. But in this case the total concentration of sodium carbonate at the start was not greater than the equivalent possible concentration of gypsum in the soil solution. That is, the amount of gypsum which could dissolve in the soil solution at any one time was sufficient to react with all the sodium carbonate present. This did not restore fertility because the salinity of the soils was too great for vegetation.

Effects of the organic treatments

On March 11 and 12, after the barley had made a good growth but before heading, the carbon dioxide in the soil atmosphere was determined, with results shown in table 5. The air analyzed was drawn from the lower central part of the soil jars.

TABLE 5

Carbon dioxide in soil atmosphere after organic and other treatments

SOIL NUMBER	TREATMENT	CARBON DIOXIDE
		per cent
15	None	0.28
16	Gypsum, all proportions	0.23—0.40
16	Stable manure	0.23
16	Green manure	0.30
16	Alfalfa meal	0.46
16	Jar 133, leached	0.33
16	Jar 132, leached and acidified	0.35
17	Gypsum, all proportions	0.25—0.39
17	Stable manure	0.40
17	Green manure	0.80
17	Alfalfa meal	1.58
18	Original or leached	0.23—0.34
19	Gypsum, all proportions	0.27—0.45
19	Stable manure	0.37
19	Green manure	1.07
19	Alfalfa meal	0.71
20	None	0.28
20	Gypsum, up to 32,000 lbs	0.23—0.34
20	Gypsum, 64,000 lbs	0.50
20	Stable manure	0.47
20	Alfalfa meal	1.03
20	Green manure	0.90

In general, the more carbon dioxide in the soil air, the better was the growth of barley on any of the soils. Apparently gypsum had no considerable effect on the amount of carbon dioxide in this air, but organic matter increased it very much, according to the nature of the organic matter. Rotted manure, being relatively inert, was least effective, while the soils treated with alfalfa meal contained the greatest amount of carbon dioxide. The increased content of carbon dioxide lowered the intensity of alkalinity so that plants were able to grow in soil which, if untreated, permitted no growth.

For the purpose of starting an alkali-sensitive crop this means of reducing the intensity of alkalinity may be of great importance. After the delicate plants

have become sturdy, they usually will endure a higher degree of alkalinity such as would recur after the lowering of the carbon dioxide when the rotting organic matter has disappeared. But for permanent reduction of total alkalinity this method is of little value.

CONCLUSIONS

Excessive salinity, which renders a soil infertile, may be removed by simple leaching with water, so that the soil will again produce good crops as shown by soil 18.

Excessive alkalinity of a soil due to sodium silicate, carbonate or bicarbonate, may be ameliorated by gypsum, to some extent, but to restore fertility it is necessary to leach the soil after adding the gypsum.

Surface application of water to pots of soil may remove so much of the alkalinity, or more especially the salinity, to the lower levels of the jar that germination and growth of plants may take place in the top soil which otherwise would be quite toxic.

Increase of carbon dioxide in the soil atmosphere lowers the intensity of alkalinity and thus permits growth of plants otherwise impossible. Such increase of carbon dioxide is readily accomplished by decay of easily decomposed organic matter.

When a soil contains 0.5 per cent or more of sodium salts, including some sodium carbonate, it is improbable that it can be made fertile by addition of gypsum in any amount, because the reaction by which sodium carbonate is changed to sulfate tends to reverse, as shown in the equation:

$$Na_2CO_3 + CaSO_4 \rightleftarrows CaCO_3 + Na_2SO_4$$

In order to prevent this reversal it is necessary to remove the sodium salts by leaching or other adequate means. On account of the low solubility of gypsum (about 0.25 per cent) it is impossible to increase its concentration in the soil solution sufficiently to prevent reversal of the above reaction in the presence of much sodium salts.

It is not feasible to leach very alkaline soils without adding some flocculating agent, such as gypsum or calcium bicarbonate, in order to prevent puddling of the soil and interference with percolation.

Water of primary alkalinity, i.e. containing sodium carbonate or bicarbonate, is not well adapted to leaching alkali soils.

When sodium chloride or sodium sulfate is removed from a saline or from an alkaline-saline soil by leaching with water, the soil is likely to show an increased intensity of alkalinity, or lower hydrogen-ion concentration, before all the sodium carbonate is removed. This was observed with all the soils used in the experiment. The intensity of such induced alkalinity may be sufficient to be toxic to some plants, but the quantity will usually be so small that a moderate amount of carbon dioxide, such as the plant sets free or such as may be generated by decaying organic matter, will reduce the intensity to a point below the toxic limit.

CERTAIN RELATIONS BETWEEN THE PROTEIN CONTENT OF WHEAT AND THE LENGTH OF THE GROWING PERIOD OF THE HEAD-BEARING STALKS

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In another paper (1) the writer has shown how applications of soluble nitrogen, applied at certain growth phases of the plants, affected the protein content and hardness of "soft white" Australian wheat. A range from 8.6 to 15.2 per cent in protein and a range from no. 2 "soft white" to no. 1 "hard spring," according to commercial grading, represented the magnitude of differences in the quality of the wheat produced. Good correlation was obtained between the differences in protein content of the wheat and the time of nitrogen applications. The treatments are fully described in the paper cited.

Very marked differences in the time of tillering of the plants and culm formation were obtained by the treatments. Plants that produced tillers or culms early, produced soft wheat, low in protein; those that tillered late produced hard wheat, high in protein. Although a relationship could be shown between the time of tillering and the quality of the wheat, it does not appear that the important physiological condition affecting the protein content of the wheat is related, as the cause, merely to the time of tillering. The important physiological condition seemed to be the length of the growing period of the tillers as head-bearing stalks. The age of the plant when tillers arose was an important factor that affected the length of the growing period of the culms. Because the length of the growing period of wheat is relatively fixed for any given environmental complex, tillers that arose late in the growing period of the plant had a shorter span of growth than those that arose earlier. The differences obtained in the time of tillering depended largely upon the time when nitrogen was applied. In this respect, the time of application of nitrogen was a condition that affected the length of the growing period of the head-bearing stalks. That this was an important factor, or set of conditions, in the production of the wheats of varying protein content, is shown by table 1.

The table shows very clearly that the length of the growing period of the head-bearing stalks was decidedly shorter in those cultures that produced the high-protein wheat than it was in those that produced the low-protein wheat. The differences for the extreme cases were 68 days. The good correlations

apparent between the differences in protein content of the wheat with that of the length of the growing period of the stalks is strong indication that the two circumstances may be related as effect and cause, respectively.

As stated in the paper cited, the culture medium employed was a soil deficient in available nitrogen and had a low crop-producing power for cereals. It was a soil that responded very quickly in increased crop production upon receiving a moderate application of nitrogen. It was observed in this investigation that the cultures which received nitrogen at the time of planting the seed grew rapidly and soon developed the culms that became the head-bearing stalks. The cultures, because of the ample supply of available nitrogen, grew into strong plants. These decidedly exceeded all other cultures in vege-

TABLE 1

Relation between the protein content of spring wheat and the length of the growing period of the head-bearing stalks, as affected by applications of nitrogen at different growth phases of the plants

NUMBER OF TRIPLICATE JAR SERIES	DATE OF PLANTING	DAYS AFTER PLANTING WHEN N WAS APPLIED	COMMERCIAL GRADE	PROTEIN CONTENT	LENGTH* OF GROWING PERIOD OF HEAD-PRODUCING STALKS	TOTAL LENGTH OF GROWING PERIOD OF PLANTS
				per cent	*days*	*days*
1	1/14/19		2 soft white	8.6	193	201
2	1/14/19	17	2 soft white	9.3	187	197
3	1/14/19	33	1 soft white	10.4	167	194
4	1/14/19	48	2 hard spring	11.8	157	194
5	1/14/19	72	1 hard spring	13.2	140	206
6	1/14/19	110	1 hard spring	15.2	125	229

* Count was begun on the day branched leaves appeared which marked the inception of stalks and tillers.

tative development during the first four weeks of growth. When, however, the plants in the other pots received their applications of nitrogen later in the growing period, they responded to the treatment to a greater degree than did the cultures that received nitrogen at the time of planting, and exceeded them in growth. As a rule, the later the nitrogen was applied, the greater and quicker was the response in vegetative growth. This response in vegetative growth consisted primarily in the formation and rapid growth of tillers. Tillering was greater in all cultures that received nitrogen 33 days or more after planting than in those that received nitrogen earlier in the growing period. The maximum tillering of all the cultures was produced in those pots which received nitrogen 110 days after planting. Nearly all the tillers of all the cultures became head-bearing stalks. The condition, therefore, that initiated tillering, within the scope of the investigation, was, in a large measure, subject to change at will, while that of maturation of the plants which concluded the growth period was not so subject.

The table shows no correlation between the length of the growing period of the plants receiving different treatments and the protein content of the wheat. It is noted, however, that the cultures which received nitrogen 33 and 48 days after planting had the shortest growing period of all in the series. This shows that applications of nitrogen to wheat plants made at certain growth phases, can shorten the total length of the growing period, and applications of nitrogen made at other growth periods of the plant can lengthen its total growing period.

In view of the results obtained, the question may arise as to what the physiological causes are that relate the protein content of the wheat to the length of growing period of the head-bearing stalks. An answer to this question at present can be only in the nature of a suggestion. It is known that the protein and carbohydrate content of wheat, in general, may vary over a considerable range. This variation may be due to genetic characteristics of the plant, or to environmental conditions of growth. Apparently the latter set of factors as the cause of variation, is of much greater importance than the former. Differences in the protein and carbohydrate contents of the wheat, as found in this investigation, obviously imply that relatively different amounts of nitrogen compounds and carbon compounds were used in the processes of assimilation. The rate of absorption of nutrients and the length of the period of absorption, that is, the length of the growing period of the plant, are two factors among others that determine how much material can be absorbed. Both the total amount of nitrogen compounds and carbon compounds absorbed by the plant and their relative proportion one to the other, apparently were factors that affected the processes of assimilation and the kinds of products assimilated.

From the standpoint of rates of absorption, it is possible to conceive of two sets of conditions that would account for the high-protein wheat obtained in the investigation. One of these would be that the rate of carbon intake to that of nitrogen was decreased in the production of high-protein wheat as compared with that of low-protein wheat; the other that the rate of nitrogen intake to that of carbon was increased. Obviously the latter set of conditions seems the more probable of the two. It seems reasonable to assume that the plants that received the applications of nitrogen late, say from 48 to 110 days after planting, had a larger supply of this nutrient for their later growing period than did those plants that received nitrogen at the time of planting. The application of nitrogen made at the time of planting was partly used up by the vigorous growing plants at the time other cultures received their application of nitrogen. Consequently, when the application was made early in the growth period, there was not so much nitrogen available in the latter growth phases of the plants, when presumably the demand for this nutrient was the greatest, as was available in those cases where the nitrogen was applied late. While the supply of nitrogen available to the plants sets the limits of the amount that possibly may be absorbed, nevertheless, the capacity of the

plants to absorb and utilize the nitrogen presumably was an important factor that affected the rate of nitrogen intake. The condition of relative insufficiency of nitrogen under which the plants that produced the high-protein wheat were started, seemed to operate as a means that gave the plants a greater capacity to absorb and utilize the nitrogen when applied late. The larger total production of dry matter and the greater protein-content of the wheat obtained from plants that had a short growing period of the stalks was assumed to indicate the relatively larger capacity for nitrogen absorption and utilization.

The length of the period of growth during which nutrients are absorbed, is a factor that may affect the amount of material taken up by the plant. If the rates of absorption of nutrients had been the same for all plants throughout the growing period, then the plants that had a long growing period should, other conditions being equal, absorb a larger amount of nutrient material than those plants of a short growing period. So far as this may be applied to the carbon dioxide intake only, wheat of a long growing period would be expected to be more starchy than that of a short growing period, as in the former case it could build up more of the carbon photosynthetic products than in the latter. But the factor of the length of the period of growth does not explain the nitrogen relation as found in these different wheats. It thus seems that the most probable explanation of the cause of the differences in protein content of this wheat is to be found in the differences in the rates of absorption of nitrogen and its utilization, which were greater in the wheat whose head-bearing stalks had a short growing period than in those which had a long growing period.

REFERENCE

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THE INFLUENCE OF GROWING PLANTS UPON OXIDATION PROCESSES IN THE SOIL[1]

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INTRODUCTION

That a symbiotic relationship exists between leguminous plants and specific strains of nitrogen-fixing bacteria was finally established only after decades of investigation. The knowledge and control of this relationship has been of great value to agriculture and it is probable, that equally important relationships exist between other groups of soil microörganisms and the growing roots of cultivated plants. Considering the physical and chemical activities involved in the growth of roots and the biochemical activity of the soil organisms in a productive soil, it appears impossible that the groups or sets of reactions involved in the life processes of such widely differing organisms could mingle so intimately and not have a marked effect upon each other. Certain types of microörganisms may function more actively upon the surfaces or in the immediate vicinity of the rootlets and root hairs of green plants than upon the particles of the soil complex not in contact with the growing roots. There is reason to believe that the oxidizing flora of the soil is thus stimulated by contact with, or by close proximity to the growing roots of the higher plants.

Carbon dioxide which is generally taken as the index of biochemical oxidation is, of course, liberated into the soil by the roots of growing green plants as well as by the organisms of decay. Therefore measurements of the carbon dioxide found in the soil atmosphere of planted and unplanted areas can be of no aid in determining whether growing plants retard or hasten the liberation of plant nutrient material as it is affected by the oxidation processes.

The experiments reported in the following pages were planned and executed for the purpose of ascertaining whether growing green plants have any influence upon the rate of oxidation of soil organic matter.

REVIEW OF LITERATURE

The literature cited bears upon the factors which cause and influence oxidation processes in the soil including the effects which growing plants have upon each other as well as upon soil biological activities.

[1] Paper No. 44 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Plant Physiology.

About the middle of the last century Boussingault and Lewy (5) observed that the decomposition of soil organic matter required more oxygen than was present in the organic matter itself. Later Schloessing (52) found that the soil atmosphere contained less oxygen and more carbon dioxide than the atmosphere above the soil. Wollny (65) carried out some extensive experiments on oxidation by measuring the amount of carbon dioxide set free by aerating a given amount of soil. He was the first to attribute the oxidation to microorganisms.

More recently Russell (48) has reported work in which he measured the amount of oxygen absorbed or utilized by soil organisms. He considered that most of the oxidizing agents were aerobic and that the oxygen absorption method gave a better index of biological activities than the method of Wollny, because considerable of the carbon dioxide liberated is adsorbed and retained by the soil.

Knowing that living cells are concerned in the process, it was but natural to expect that enzymatic action plays a part. The presence of active oxidase and peroxidase in soil has been reported by Woods (66) and Koenig (27), while Schreiner and Reed (53) have shown that growing roots can cause considerable oxidation which they attribute to the extracellular action of oxidase. Schreiner and Skinner (54) have pointed out that the soil oxidation activities not only liberate large quantities of plant nutrient material but that they are also necessary for converting toxic substances into harmless and beneficial compounds.

Several investigators have studied the influence which various materials have upon the oxidizing power of the soil. Lemmerman and his associates (32) report the influence of calcium carbonate. Lipman and Blair (35) ascertained the effect of adding nitrates and carbohydrates to the soil while Fred and Hart (14) compared the effects of sulfates and phosphates. Others who have included carbon-dioxide determinations in their soil researches are Potter and Snyder (46, 47), Van Suchtelen (62), Gainy (15) and Neller (43, 45).

For many years it has been observed that in a mixed growth of legumes and non-legumes the latter appear to grow better than they do when planted alone. After it became known that the growth of legumes increased the nitrogen content of the soil it was suggested that the non-legumes were able to utilize some of the nitrogen during the same season that it was being fixed in the root tubercles of the legumes.

By means of a system of porous and non-porous cups Lipman (33) demonstrated that growing peas exerted a beneficial influence upon the growth of oats. Further investigations upon the nitrogen content of the plants as well as upon the effect of adding sodium nitrate made it apparent that nitrogenous compounds passed out of the roots of at least some legumes and became available to non-legumes associated with them.

Lyon and Bizzell (36) report field experiments in which it was found that timothy grown with alfalfa or red clover contained a greater percentage of

nitrogen than timothy grown alone. Since the rate of nitrification of ammonium sulfate was greater in the alfalfa soil, they suggested that the favorable effect upon the non-legume was due to a more rapid formation of nitrates where legumes were growing. Westgate and Oakley (64) consider that their results conflict with those of Lyon and Bizzell since they found that an increasing amount of wheat planted with clover decreased the protein content of both wheat and clover.

Kellerman and Wright (23) did not find any increase in the nitrifying power of a semi-arid soil previously planted with legumes. They point out that the effect of a crop upon the nitrifying power may be very different in different soils. It seems evident, however, that non-legumes generally benefit from an association with legumes provided the soil and climatic conditions are normal.

In England the peculiar and decidedly toxic effect of grass grown in conjunction with fruit trees has been quite conclusively demonstrated by Bedford and Pickering (2) who consider that the toxin results from the dead organic matter of the grass roots and that it is rendered harmless by oxidation. This is in accord with previous work by Schreiner and Skinner (54) who found that the harmful influence of a soil extract may be removed by processes which promote oxidation.

The effect of plant life upon the oxidizing power of the soil has been given less attention than its effect upon the nitrifying power. This, probably has been due to the fact that the question of nitrates has been a pressing one and also because it is difficult to measure the rate or determine the nature of oxidizing reactions. Schreiner and Sullivan (55) found that the potential oxidizing power of the soil determined by shaking its water extract with a solution of aloin was increased by 75 per cent as a result of 17 days' growth of wheat. The effect upon a poor, sandy soil, however, was not so pronounced as it was upon one which was manured and more productive.

In some recent studies of the soil atmosphere, Russell and Appleyard (51) concluded that the effect of a growing crop was to increase the carbon dioxide content of the soil atmosphere. They are in doubt as to whether or not the growing crop might be credited with any stimulating effect upon bacterial activity, but do consider that there is not much evidence of a depressing effect such as Russell mentioned previously (49). Turpin (61) states that the carbon-dioxide production in a cropped soil was markedly greater than that in a soil in which no crop was growing. It was concluded that the excess carbon dioxide in a cropped soil is due to the respiratory activity of the plants rather than to the decay of the root particles from the crop growing on the soil at the time of the analysis.

Turning now to the question of the effect of crops upon nitrate production, it may be found that although a considerable number of investigators have studied the subject they differ widely in their conclusions. Lawes, Gilbert, and Warington (29) were among the first to record this apparent influence of

crops. They state that the nitrogen of unmanured land nitrifies with more difficulty than the nitrogen of land that has yielded large crops.

Later King and Whitson (24) found that the nitrate used by crops (tops only) indicated either a greater nitrification of the original soil organic matter where legumes were growing or that the legumes utilized considerable nitrogen directly from the air during the growth of the plant. The following year they reported a more definite experiment (25). The nitrogen in a crop of oats and the soil nitrate to a depth of 4 feet were determined on June 20. One-half of the oats were then harvested. Nineteen days later the nitrates in both halves of the plot were determined. It was found that the nitrogen utilized by the crop during the 18-day interval plus the nitrogen of the soil nitrates was about twice as great as the nitrogen of the accumulated nitrate on the bare portion of the plot. Had the nitrogen of the roots been considered, the apparent increased nitrification in the cropped soil might have been still greater. The authors could give no explanation for the marked increase. Fraps (13) reports a somewhat similar result with maize grown in a greenhouse, except that the soil was uncropped from the beginning of the growing season. However, great variations in the moisture and aeration conditions occurring in his tests might have caused the increase in nitrate production in the cropped soil.

Lyon and Bizzell (37) found more nitrates in land upon which maize was grown than in a similar unplanted soil. But during the later periods of growth there was less nitrate accumulation than in the cropped soil. They advance the theory that the growing maze stimulates the formation of nitrates at first and later inhibits it when the roots cease to grow and begin to decay. These authors found (39) that even after an alfalfa soil had been kept fallow for 2 years, it nitrified dried blood more rapidly than did a timothy soil similarly treated. They also report some recent work (40) in which six lysimeters were planted with clover and six with timothy. Oats and maize were planted the following year and the total production of nitrates was determined for each lysimeter. Those which contained the clover soil caused the greater production of nitrates in spite of the fact that ample quantities of dried blood were added to each soil. However, the increased nitrate production in the clover soil may have been due to the fact that the clover roots were more easily nitrified than the dried blood.

It is interesting to note that several investigators have found that the nitrate production under a cultivated crop such as corn or potatoes is higher than under an uncultivated crop such as wheat, oats, or timothy. Such were the findings of Jensen (21) in South Dakota, Brown and MacIntire (7) in Pennsylvania, Ladd (28) in North Dakota, and Lyon and Bizzell (38) in New York. These results appear to obtain chiefly in prairie soils which are generally well supplied with humus. Here more frequent cultivation would probably cause a more intensive nitrification.

The semi-arid soils of the United States present a set of conditions much different from those of the humid regions, and Stewart and Greaves (58) report that the nitric nitrogen in corn and potato land and in fallow land was high in the spring and summer but comparatively low in the fall, while the nitric nitrogen of alfalfa land was low throughout the year. A later report from Utah (17) concludes that alfalfa not only feeds more closely upon the nitric nitrogen of the soil than do other crops, but that it also increases the nitrifying power of the soil. McBeth and Smith (41) were led to conclude that the nitrifying power of a cropped and irrigated soil was higher than that of one which was not cropped.

As opposed to the conclusion that crops stimulate nitrification in the soil, a number of investigators have obtained experimental evidence that growing crops have no influence upon nitrification or produce a retarding effect upon this process. Deherain (11) concluded that if moisture conditions were always the same and if no loss occurred through drainage the nitrate production would be the same in both fallowed and cropped soils. Vorhees, Lipman, and Brown (63) found that nitrate accumulation was slower under oats and clover than it was in fallow soils. Taking into account the nitrate nitrogen used by the crops and that remaining in the soil Russell (49) concluded that less nitrate nitrogen was produced in cropped than in uncropped soils. However, in his later studies (51) of the soil atmosphere he found no evidence of any depressing effect of crops upon nitrate production.

In India, Leather (30) determined the nitrate nitrogen in a soil from which the previous accumulation of nitrates had been leached by a heavy rainfall and found that less nitrate was produced in this soil where grass was growing upon it than where no vegetation occurred. Kellerman and Allen (22) state that in their irrigated soils the age and condition of an alfalfa field bore little if any relation to the potential rate of nitrification.

Berthelot (3) was probably one of the first to observe the effects of growing crops upon bacterial activities other than those of the nitrifiers. He states that there was less rapid fixation by free living organisms in cropped than in uncropped soils but considers that this may have been due to the fact that the plants used some of the fixed nitrogen. On the other hand, Heinze (19) found that the practice of fallowing increased the nitrifiers, ammonifiers and azofiers.

Caron (8) reports that a greater number of organisms were present under clover than under grain crops. Stoklasa and Ernst (59) counted from seven to eight millions of colonies per gram of clover soil, while comparable figures gave five to six millions in barley soil and one to two millions in soil growing sugar beets. Leclair (31) also found higher bacterial numbers under cowpeas than in soil of fallow plots. An increase in bacterial numbers and in the nitrifying and ammonifying power of soil under rotation cropping as opposed to continuous single-cropping systems are the results submitted by Brown (6).

Thus the evidence appears to show that growing crops do not exert a depressing effect upon biological activities in soil. Neither does it seem definitely proven that they exert a stimulating effect, and to clear up the matter there is need of comprehensive experiments under conditions of better control than those which have so far been reported. Russell (50) realized such a need when he recently stated, "there appears to remain only the possibility that the growing crop has a direct influence upon the decomposition processes going on in the soil. Unfortunately field experiments alone do not enable us to decide this question and the systematic laboratory investigation has still to be undertaken."

PRINCIPLES INVOLVED IN THE EXPERIMENTAL WORK

These experiments were planned for the purpose of ascertaining the influence of growing roots upon oxidation activities that take place in soil. This was done by comparing two lots of the same sample of soil, the one planted and the other unplanted, with all other conditions such as moisture, aeration, and supply of plant nutrients as nearly as possible the same for each soil.

The amount of carbon dioxide evolved from a soil is an index of oxidation activities occurring therein. Under normal conditions, of course, a part of the carbon dioxide produced in a soil is due to the respiration of growing plants and a part to the activities of microörganisms. The conditions of the experiments required that the latter source of production be accurately measured. This was accomplished by placing the soil and growing plants in enclosed systems through which air, freed from carbon dioxide, was drawn. Thus the only source of carbon dioxide was that set free by the decomposition processes taking place in the soil contained within the systems. The carbon dioxide thus utilized by the growing plants in the photosynthetic processes and that respired, was first produced by the microörganisms of the soil in which the plants were growing.

The total carbon dioxide evolved in the enclosed systems without plants was determined by means of passing a slow but continuous current of carbon-dioxide-free air into the systems and then out again through absorption towers in which the carbon dioxide was retained and could be measured. In the systems containing growing plants, some of the carbon dioxide evolved from the soil was, of course, fixed by the plants in the process of photosynthesis and retained. This fixed carbon dioxide was determined by making a total carbon analysis of the plants. Thus the total amount of carbon dioxide produced by microörganisms in planted and unplanted soils was measured quantitatively.

DESCRIPTION OF APPARATUS

The apparatus with which most of the work was done consisted of twelve separate units, each of which employed a glazed earthenware jar *A* (fig. 1) to which was cemented a square board *B* by means of shellac. This served as a base for an inverted battery jar *C* which was

22 cm in diameter and 30 cm high The center of the board was removed to correspond to the inner diameter of the glazed jar and was grooved on its upper surface to receive the lower edge of the inverted battery jar After having been sealed to the lower jar the wooden base was thoroughly impregnated and coated with hot paraffin wax.

The air which was drawn into the apparatus was freed from carbon dioxide by passing it through a tube 22 mm in diameter and 330 cm long, lying in a horizontal position and loosely filled with 4-mesh soda lime (made up in a moist condition for carbon-dioxide determinations). From thence it was bubbled through a 10 per cent sulfuric acid solution contained in each of the twelve distributing bottles *D*. The acid solutions in the distributing bottles

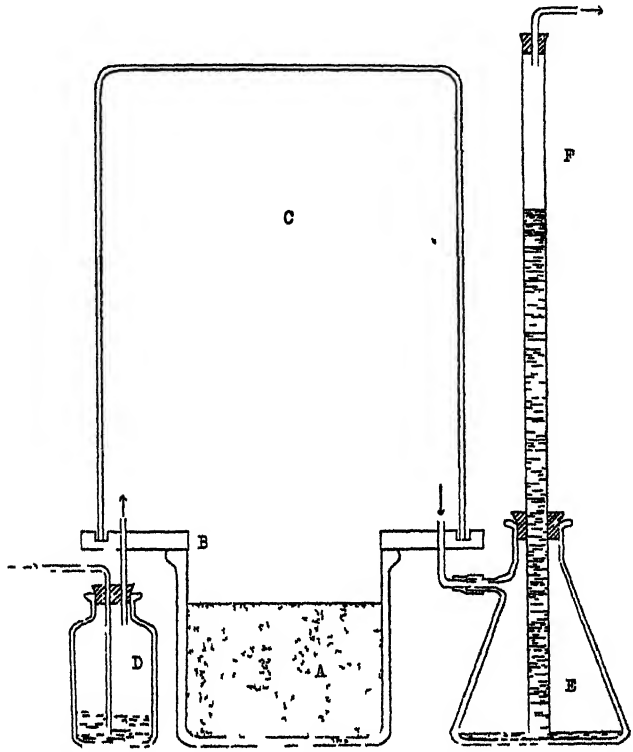

FIG. 1. DIAGRAM REPRESENTING A SECTION THROUGH ONE OF THE UNITS OF THE APPARATUS USED IN DETERMINING THE CARBON DIOXIDE EVOLVED FROM THE SOIL CULTURES

prevented diffusion of carbon dioxide from one unit to another. The outdrawn air from each unit was led through a modified Truog (60) absorption tower *E*. Slow but continuous aspiration was maintained by means of a suction pump which was supplied with water from a constant level tank. Figure 1 of plate 1 shows the twelve units as seen from the front or outlet side. Figure 2, the rear view, shows how the indrawn air was distributed to each unit.

The tendency to create a partial vacuum within the apparatus was very slight, being approximately equivalent to the 3-cm columns of solution contained in the distributing bottles. The main difficulty in the way of keeping each system air-tight was in the unequal expansion and contraction of the apparatus caused by the fluctuating temperature of the greenhouse. This unequal expansion and contraction was especially marked between the inverted battery

jar *C* (fig. 1) and the wooden base *B*. Molten paraffin was first used to fill the circular groove and thus seal the jar to its base. This allowed leaks to occur after a time because the expanding and contracting glass caused the paraffin to be pushed away from its inner wall. Vascline failed to prevent leakage for much the same reason.

Neither sealing wax nor shellac could be used because it was necessary to remove the jars from time to time. A wax was needed which would adhere to the glass and be elastic enough to withstand the expansion and contraction without rupturing. To meet these requirements various mixtures of rubber, beeswax, paraffin and vaseline were tested. The wax finally used was made by melting down old rubber stoppers with a very small amount of paraffin. A small amount of sulfur was added and the heating continued under a hood until the mixture had the desired melting point. It was found that the consistency and the melting point limits were determined largely by the amount of heating and so a definite formula for the mixture can not be given. With the use of this wax the apparatus was kept practically free from leakage, but not without constant care and attention.

EXPERIMENTAL PROCEDURE

The sand and the soil which was used as a culture medium was put through a 3-mm. sieve and weighed out into 2000-gm. lots, one for each of the jars of the apparatus. When pure sand or a soil deficient in humus was employed it was thoroughly mixed with a definite amount of organic matter. This consisted of a humus preparation made by mixing finely ground alfalfa hay with soil diluted with sand. This mixture was moistened and occasionally stirred for about two weeks, by which time the more easily decomposable portions had become oxidized. It was then dried at 100°C. and stored for future use.

Seedlings were germinated in paraffined drinking cups containing some of the same lot of soil which was used in the jars to which they were transplanted. By this method all of the soil in the cups could be transferred to the apparatus without greatly disturbing the roots of the growing plants. Cups of similarly treated unplanted soil were transferred to the jars used as checks.

As soon as the seedlings were transplanted, the required amount of water or of nutrient solution was added to the solid substratum and the jars were sealed. A slow but continuous current of air was then started through the systems and the carbon dioxide which was not fixed by the plants in the photo-synthetic processes was absorbed in the barium hydroxide towers. The total carbon dioxide absorbed in these was determined quantitatively after shaking the glass beads out of the tube *F* (fig. 1) into the flask *E* containing the residual barium hydroxide, rinsing the tube with carbon-dioxide-free water and then titrating the residual barium hydroxide with oxalic acid, phenolphthalein being used as the indicator. A complete refilling of the towers was necessary every 1 to 3 days. On several occasions the barium hydroxide in some of the towers became neutralized during the night hours, thus involving the possibility of a slight loss of carbon dioxide. But since special precautions were taken to avoid such occurrences it is considered that the error thus occasioned was negligible.

Since the plants were grown in an enclosed space the atmosphere surrounding them was approximately saturated with moisture during the greater part of the growth period. This, of course, checked transpiration and affected the growth of the plants in much the same way as that described by Eberhart (12). The stems were longer and smaller in diameter and the leaves were somewhat smaller than those of plants grown in drier air. Newcomb and Boverman (42) working with seedlings in the dark found that growth in unventilated chambers was not retarded. In the present work good growth was obtained and the plants appeared vigorous and healthy except in one or two instances when some of the plants were injured by too high temperatures in the summer months.

The carbon-dioxide content of the air surrounding the plants was considerably higher than that of atmospheric air at the beginning of the experiments, but was probably lower at their termination about 30 days later. It has been reported by Boussingault (4) and later

by Cummings and Jones (10) that the most rapid plant growth takes place in an atmosphere containing about 8 per cent of carbon dioxide.

When it was desired to terminate an experiment, air was drawn through the systems rapidly for two or three hours in order to remove the carbon dioxide as completely as possible. The plants were then removed and analyzed for carbon. It was impossible to separate all of the finer rootlets from the soil. A slight growth of algae was observed on the surface of the soil in the jars, but as this occurred on both the planted and unplanted soil it is not probable that the comparative results were appreciably altered. In some cases weed growth developed in the unplanted jars, in which event they were harvested and the carbon dioxide, as represented by their total carbon content, was added to the amount obtained in the absorption towers for those jars.

All the plants from each culture were dried to constant weight at 104°C., weighed and ashed. The loss by ignition minus that of an equal number of seedlings of approximately the same size as those planted, was taken to represent the amount of dry plant material produced during the period of the experiment. In order to reduce any possible error the seedling blank was obtained by burning from three to four times the number of seedlings which were planted in one jar and calculating for the required number. The carbon determinations were made according to the official method of the Association of Agricultural Chemists (1).

It is known, of course, that the ash of plants contains carbonates the carbon of which should be included as part of the total carbon of the plant. This was not done in the present experiments. However, if this carbon of the ash had been considered in the present work, the results obtained would have been even more positive. Therefore, it cannot be considered that the error thus introduced could detract from the results obtained.

INFLUENCE OF GREEN PLANTS UPON THE OXIDATION OF ORGANIC MATTER MIXED WITH SAND

A washed white sand having a maximum water-holding capacity of 30 per cent by the Hilgard method (20) was inoculated by mixing it with 10 per cent of its weight of a fertile loam soil. Two thousand grams were used per jar with which 3 gm. of finely ground soybean hay were thoroughly mixed. Six soybean seedlings, 10 days old, were planted in each of the jars numbered 11 and 12 (table 1) and the soil in all of the jars was then moistened to 50 per cent of its water-holding capacity with a nutrient solution. The inverted battery jars were then sealed down and aspiration of air free from carbon dioxide started through them on November 12, and continued for the next 29 days. By that time many of the upper leaves were pressing against the tops of the enclosing jars.

The data of table 1 clearly show that the total carbon dioxide recovered from each of two planted jars was considerably more than the total amount obtained from the corresponding unplanted jars, the average for the latter being 1737.0 mgm. and for the former 2093.4 mgm. The average total carbon dioxide evolved from the planted jars is thus 12.1 per cent higher than the average total yield from the unplanted jars. It appears, therefore, that the growing plants exert a pronounced accelerating influence upon the oxidation activities taking place in the sand cultures. It is interesting to note in this connection that in some preliminary work (43) previously carried out in a similar manner, the influence of plants growing in sand cultures was even more pronounced

than that here shown, the average total amount of carbon dioxide recovered from jars planted with wheat and from those planted with barley being 25.2 per cent and 12.9 per cent higher, respectively, than the corresponding amount recovered from the unplanted jars.

TABLE 1

Effect of soybeans on the oxidation processes in sand to which equal amounts of soil and organic matter were added. Experiment conducted from November 12 to December 10, 1919

	Intervals between titrations	Check (no plants)		Soybeans	
		Jar 9	Jar 10	Jar 11	Jar 12
	days	*mgm.*	*mgm.*	*mgm.*	*mgm.*
CO_2 withdrawn from system	0–3	252.6	227.0	253.4	288.0
	4–5	165.5	167.0	167.0	167.0
	6–7	167.0	167.0	101.4	167.0
	8–9	161.9	159.5	129.0	167.0
	10–11	170.1	244.9	260.9	154.9
	12–14	196.5	221.4	76.2	54.9
	15–16	147.6	150.0	69.5	150.0
	17–21	165.0	178.8	15.0	69.2
	22–26	132.9	153.4	14.0	23.7
	27–29	149.6	96.3	48.4	47.2
Total		1708.7	1765.3	1134.8	1288.9
Dry weight of crop				1278.7	1188.5
Ash in crop				239.3	246.9
Organic matter in crop				939.4	941.6
Organic matter in seedlings				430.0	430.0
Organic matter produced during experiment				509.4	511.6
CO_2 fixed by plants during experiment				879.7	883.5
Total CO_2 obtained from soil		1708.7	1765.7	2014.5	2172.4
Average CO_2 obtained from soil		1737.0 mgm.		2093.4 mgm.	
Average increase over check				12.1 per cent	

TABLE 2

Moisture content of cropped and uncropped soils kept under enclosed systems

	Experiment 1 November 2 to December 10				Experiment 3 November 27 to December 27			
	Uncropped jars		Cropped jars		Uncropped jars		Cropped jars	
	1	2	1	2	1	2	1	2
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Initial moisture content	15.0	15.0	15.0	15.0	24.0	24.0	24.0	24.0
Final moisture content	13.6	14.2	11.2	12.4	22.3	20.3	22.4	21.3

The apparatus by means of which the first experiment was conducted was equipped with calcium chloride tubes to permit a measurement of the amount of water lost from the enclosed jars of sand. It was found by weighing the

tubes as well as by making moisture determinations of the sand at the close of the experiment that only a slight loss of moisture occurred. This is indicated in table 2 which shows also that when soil was used there was no appreciable loss of moisture. It may be concluded, therefore, that differences observed in the total carbon dioxide evolved from the planted and unplanted soils were not caused by variations in their moisture contents.

INFLUENCE OF GREEN PLANTS UPON THE OXIDATION OF ORGANIC MATTER IN A LOAM SOIL

No additional organic matter was added to the soil used in this experiment. It contained 1.218 per cent of organic carbon and had a maximum water-hold-

TABLE 3

Effect of buckwheat and of field peas upon the oxidation processes in a loam soil. Experiment conducted from November 29 to Decembe 30, 1919

	INTERVALS BETWEEN TITRATIONS	BUCKWHEAT		CHECK (NO PLANTS)		FIELD PEAS	
		Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
	days	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
CO_2 withdrawn from system	0–3	88.9	85.0	81.7	74.6	112.3	112.3
	4–5	23.9	15.8	46.5	34.2	55.1	47.6
	6–7	76.7	61.1	33.0	38.9	25.1	38.0
	8–10	39.7	6.5	32.0	21.7	37.3	33.7
	11–13	49.0	21.8	58.3	58.1	55.0	36.8
	14–18	79.6	40.0	41.4	46.8	7.9	10.5
	19–23	44.4	46.0	69.3	43.0	22.0	62.1
	24–32	27.0	20.1	121.0	79.7	22.1	15.8
Total		429.2	296.3	483.2	397.0	336.8	356.8
Dry weight of crop		786.8	842.8			1032.5	1024.6
Ash in crop		347.0	367.0			317.9	405.2
Organic matter in crop		439.8	475.8			714.6	619.4
Organic matter in seedlings		92.7	92.7			416.7	416.7
Organic matter produced during experiment		347.1	383.1			297.9	202.7
CO_2 fixed by plants during experiment		561.3	619.5			418.7	327.8
Total CO_2 obtained from soil		990.5	915.5	483.2	397.0	818.5	684.6
Average CO_2 obtained from soil		953.1 mgm.		440.1 mgm.		751.6 mgm.	
Average increase over check		116.5%				70.8%	

ing capacity of 37.5 per cent. It was nearly neutral in reaction as the pH value of its water extract was 6.7 determined colorimetrically according to the method of Gillespie (16) and with the indicators described by Clark and Lubs (9). When ready for use, the soil was brought to one-half of its maximum water-holding capacity by the addition of Shive's (56) solution no. R5C2 at 1.75 atmospheres concentration. Buckwheat and field pea seedlings were

transplanted, six plants to each jar, on November 29 and harvested on December 30.

The recovery of carbon dioxide is given in table 3. Jars in which buckwheat was growing showed an increase of 116.5 per cent over the amount obtained from the unplanted jars; field peas produced a corresponding increase of 70.8 per cent.

A few months later some of the same lot of soil was tested in a similar manner except that soybeans were used instead of field peas and buckwheat. In this test, also, the growing plants exerted a stimulating influence upon the

TABLE 4

Effect of soybeans on the oxidation processes in a loam soil. Experiment conducted from May 24 to June 16, 1920

	INTERVALS BETWEEN TITRATIONS	SOYBEANS			CHECK (NO PLANTS)		
		Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
	days	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
CO_2 removed from system	0–6	206.2	136.2	235.2	399.4	394.9	340.2
	7–10	149.0	106.8	207.0	225.1	199.8	209.8
	11–14	137.5	77.0	165.3	210.0	93.7	156.9
	15–17	144.9	123.2	199.2	228.8	228.8	122.8
	18–24	280.5	175.1	232.2	455.8	263.4	328.2
Total		918.1	618.3	1038.9	1513.1	1174.6	1157.9
Dry weight of crop		1402.0	1764.8	1547.8			
Weight of ash		227.8	625.5	320.3			
Organic matter in crop		1124.2	1139.3	1227.5			
Organic matter in seedlings		425.0	425.0	425.0			
Organic matter produced during experiment		699.2	714.3	802.5			
CO_2 fixed by plants during experiment		1201.9	1227.9	1379.5			
Total CO_2 obtained from soil		2120.0	1856.2	2418.4	1513.1	1174.6	1157.9
Average CO_2 obtained from soil		2128.2 mgm.			1281.8 mgm.		
Average increase over check		66.0%					

oxidation activities of the soil. Table 4 shows that the carbon dioxide evolution, averaged from triplicate determinations, was 66.0 per cent higher than the corresponding amount obtained from the unplanted soil.

THE INFLUENCE OF RECROPPING UPON OXIDATION PROCESSES IN THE SOIL

In this experiment the same jars of sand which were used in the first experiment were replanted with wheat and soybeans, the check soils always remaining unplanted. A comparison of table 1 with table 5 shows that the second crop of soybeans appeared to have much greater accelerating influence than the first crop upon the oxidation activities taking place in the sand medium

in which the plants were grown. Table 5 shows the average total carbon dioxide recovered from the cultures planted with wheat and from those planted with soybeans to be 100.9 per cent and 108.8 per cent higher, respectively, than the average amount recovered from the check cultures.

An augmented effect of the second crop upon oxidation activities was also obtained with the loam soil previously used. The total carbon dioxide re-

TABLE 5

Effect of the second crop of wheat and of soybeans upon the oxidation processes in sand cultures. Experiment conducted from December 18 to January 10, 1920

	INTERVALS BETWEEN TITRATIONS	WHEAT		CHECK (NO PLANTS)		SOYBEANS	
		Jar 7	Jar 8	Jar 9	Jar 10	Jar 11	Jar 12
	days	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
CO_2 removed from system	0–3	191.1	191.1	191.1	181.1	191.1	182.1
	4–6	187.0	187.0	175.5	187.0	187.0	187.0
	7–9	108.9	170.0	178.0	97.1	89.4	167.0
	10–12	129.7	143.4	83.0	109.2	135.2	94.2
	13–14	40.6	43 8	68.1	51.0	65.5	55.0
	15	84.7	99.4	165.1	107.0	95.9	123.0
	16–19	48.0	75.0	108.1	116.0		24.9
	20–24	21.8	50.5	326.3	349.0	36.8	43.4
Total		811.8	960.4	1295.3	1098.3	780.9	876.6
Dry weight of crop		1280.8	2756.5			1442.5	1523.6
Ash in crop*		220.0	1916 0			394.0	424.2
Organic matter in crop		1080.8	840.5			1048.5	1099.4
CO_2 used to produce organic matter in crop		1747.4	1359.1			1695.4	1783.9
CO_2 used to produce organic matter of seedlings		26.9	26.9			69.5	69.5
CO_2 fixed by plants during experiment		1702.8	1332.2			1625.9	1714.4
Total CO_2 obtained from soil		2514.4	2292.6	1295.3	1098.3	2406.8	2591.0
Average CO_2 obtained from soil		2403.6 mgm.		1196.8 mgm.		2498.9 mgm.	
Average increase over check		100.9%				108.8%	

* Including also the soil grains which adhered to roots.

covered from this soil when replanted with soybeans was 106.6 per cent greater than that obtained from the unplanted jars, as is indicated in table 6. For the first planting the corresponding increase was only 66 per cent. In this connection it should be noted that the soil which was used to support the first crop was not allowed to become dry before the second crop was planted. This immediate replanting may have had something to do with the increased percentage of carbon dioxide recovery over that recovered during the growth of the first crop.

RESULTS OBTAINED FROM THE USE OF AN UNPRODUCTIVE SOIL

In this experiment a soil was used which was very unfavorable to plant growth, due to previous annual applications of ammonium sulfate only. Although the pH value of the water extract of this soil was 4.4, the barley seedlings which were planted in it grew fairly well for a time as is indicated by the data of table 7. The soil had about the same water-holding capacity as that

TABLE 6

Effect of a second crop of soybeans upon the oxidation processes, loam soil. Experiment conducted from June 18 to July 19, 1920

	INTERVALS BETWEEN TITRATIONS	CHECK			SOYBEANS		
		Jar 1	Jar 2	Jar 3	Jar 4	Jar 5	Jar 6
	days	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
CO_2 removed from system	0–2	257.8	93.2	176.4	244.4	144.5	116.0
	3–4	296.0	378.9	326.2	365.7	203.0	378.8
	5–6	208.2	208.2	146.6	138.8	159.5	224.5
	7–9	483.0	208.2	465.0	228.7	94.1	109.9
	10–11	341.2	200.9	207.8	256.9	134.3	138.9
	12–14	208.2	179.4	199.0	138.9	131.7	120.2
	15–18	184.7	150.6	165.8	143.2	75.2	143.6
	19–21	208.0	224.9	192.6	217.8	99.0	135.5
	22–24	89.6	91.5	79.2	150.4	93.3	144.6
	25–27	194.3	113.6	139.5	125.2	99.8	144.6
	28–31	185.6	123.4	129.6	162.4	133.5	90.9
Total		2059.1	1972.8	2223.7	2172.4	1367.9	1747.6
Organic matter in crop				59.9	2268.3	1400.0	2066.2
Organic matter in seedlings					155.5	155.5	155.5
Organic matter fixed during experiment				59.9	2112.8	1244.5	1910.7
CO_2 fixed by plants during experiment				106.4	3648.8	2149.3	3299.8
Total CO_2 obtained from soil		2659.1	1972.8	2330.1	5921.2	3517.2	5047.4
Average CO_2 obtained from soil		2320.7 mgm.			4795.2 mgm.		
Average increase over check					106.6%		

used in the preceding experiments. Since it was deficient in organic matter 20 gm. of the prepared humus previously described was added to each 2000 gm. of the soil. The data of table 7 show that the growth of barley even in this soil produced considerable increase in the amount of carbon dioxide recovered as compared with the unplanted checks, although this excess of 29 per cent is not nearly so marked as it is in some of the other experiments. It should be stated here that considerable weed growth appeared in the unplanted cultures and this, in a measure, served to offset the difference in the amounts of carbon dioxide recovered from the planted and unplanted soils.

DISCUSSION

Quantitative measurements of the total carbon dioxide liberated by the oxidation processes taking place in the soil during the period of plant growth have shown that much more rapid oxidation takes place in soil in which plants are growing than in an uncropped soil kept uuder the same conditions of moisture, aeration, temperature, etc. This indicates that the growing roots

TABLE 7

The effect of barley on the oxidation processes in an unproductive soil. Experiment conducted from June 18 to July 19

	INTERVALS BETWEEN TITRATIONS	BARLEY			CHECK (NO PLANTS)		
		Jar 7	Jar 8	Jar 9	Jar 10	Jar 11	Jar 12
	days	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
CO_2 removed from system	0–2	112.6	103.9	88.6	242.1	222.0	193.1
	3–4	83.2	270.6	65.2	240.0	330.0	367.2
	5–7	99.6	134.3	105.3	182.0	290.2	161.0
	8–10	138.9	132.9	101.0	474.0	187.2	361.9
	11–12	112.2	219.9	126.6	249.2	208.2	268.7
	13–15	128.0	121.2	91.9	143.7	168.2	150.7
	16–19	166.0	127.7	92.4	159.3	162.1	206.9
	20–22	108.8	143.5	92.4	158.4	86.2	202.0
	23–25	111.4	194.0	48.2	108.0	136.9	107.1
	26–28	134.9	46.5	129.1	96.7	104.5	117.9
	29–32	128.3	70.0	124.0	98.8	115.6	114.8
Total		1323.9	1563.9	1064.7	2152.2	2011.1	2251.3
Organic matter in crop		1255.5	1358.0	1374.5	*313.8	210.7	147.4
Organic matter in seedlings		217.2	217.2	217.2			
Organic matter produced during experiment		1038.3	1140.8	1157.3	*313.8	210.7	147.4
CO_2 fixed by plants during experiment		1827.4	2007.8	2036.9	552.3	370.3	259.4
Total CO_2 obtained from soil		3151.3	3571.7	3101.6	2704.5	2381.9	2510.7
Average CO_2 obtained from soil		274.9 mgm.			2532.4 mgm.		
Average increase over checks		29.0%					

* Organic matter of weed growth in the unplanted jars.

exert a direct influence upon the oxidation processes taking place in the medium in which they are growing.

It is known, of course, that soil oxidation processes are largely due to biological activity. It is also recognized that such activity results in the production of quantities of available plant nutrients, both directly through the nitrification of soil organic matter, and indirectly through the increased dissolving power of a more highly carbonated soil solution. Thus any stimulus given to the oxidizing processes in the soil would naturally tend to increase the available plant nutrients and this in turn should stimulate plant growth.

That such a stimulus is given to the oxidizing processes in the soil is clearly brought out by the quantitative experimental data above presented. It is therefore reasonable to suppose that a symbiotic relationship may exist between the growing plants and the oxidizing organisms in the soil.

Russell (50) has suggested that growing plants may exert a direct influence upon biological activity taking place in a soil. The present experiments support this suggestion in so far as biological oxidation is concerned. However, the direct cause of the stimulating influence of the growing plants upon the oxidizing processes in the soil is not at all clearly understood and any attempted explanation can only be suggestive. It is well known, of course, that the root hairs which develop on growing roots function only a few days and then die while new ones are continually being formed. Large numbers of other cells and cell aggregates are also continually being sloughed off from the roots growing in the soil.

All of this cast-off material undoubtedly oxidizes very rapidly, although Knudson (26), who studied the viability of root cells detached during plant growth in solution cultures, has shown that such detached cells may remain alive from 40 to 50 days. In the soil, however, the conditions for rapid oxidation are much more favorable and there is good reason to believe that this cast-off organic material decomposes rapidly. All such cast-off organic material which is continually being supplied by the plants during the active growing period apparently furnishes readily available energy to the soil microörganisms involved in the oxidation processes. It is entirely possible that this readily available energy together with excretions from the growing roots may stimulate the oxidizing organisms in such a way as to bring about a more rapid and a more complete decomposition of the previously deposited organic matter. All the experimental evidence here brought forth points to such a conclusion.

SUMMARY

Experiments were conducted to determine the influence of growing plants upon the oxidation activities taking place in soil and specially prepared sand cultures. Quantitative measurements of the total carbon dioxide liberated from the soil or sand cultures were here taken as the index of the oxidation activities. Special apparatus was devised by means of which the total carbon dioxide liberated by the oxidation processes taking place in the substrata employed during the periods of plant growth could be measured quantitatively. This involved the complete exclusion of atmospheric carbon dioxide. That portion of the total carbon dioxide (evolved from the soil) which was fixed by the plants in the photosynthetic processes was determined by analyses of the plants for total carbon. The remainder of the total carbon dioxide was retained in absorption towers containing barium hydroxide and was quantitatively determined.

1. The oxidation processes in sand cultures to which organic matter was added were accelerated by growing green plants, the average total carbon dioxide recovery from the planted cultures being 12.1 per cent higher than that from the unplanted check cultures.

2. Growing plants very greatly increased the oxidation processes in a soil of average productiveness as indicated by the total carbon dioxide produced. The average total amounts of carbon dioxide recovered from cultures planted with buckwheat, field peas, and soybeans were 116.5 per cent, 70.8 per cent, and 60.0 per cent greater, respectively, than were the corresponding amounts recovered from the unplanted check cultures.

3. During the growth of a second crop of soybeans on the same soil, the increase in the oxidation activities over those exhibited in the unplanted soil was more pronounced than it was during the growth of the first crop.

4. All the experimental evidence obtained indicates that growing plants of buckwheat, barley, soybeans, and field peas have a beneficial influence upon oxidation activities in the substrata in which the plants were grown and suggests a symbiotic relationship between the soil-oxidizing organisms and the growing green plants.

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PLATE I

FIG. 1. A view of the front or outlet side of the apparatus used to determine the influence of plants upon the oxidation activities in the soil. Twelve barium hydroxide towers were used for recovering carbon dioxide from air removed while soda lime in the long horizontal tube, lying on the table, freed the indrawn air from carbon dioxide. The six central jars contain barley and soybean plants.

FIG. 2. A view of the rear of the apparatus showing the twelve distributing bottles containing dilute sulfuric acid solutions. The circular grooves into which the inverted battery jars are sealed may also be noted.

FIG 1

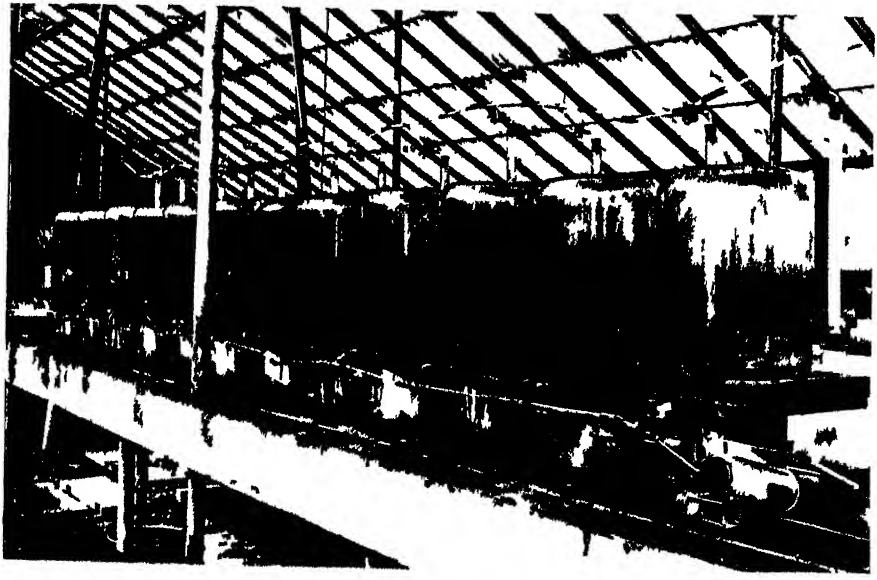

FIG 2

PRELIMINARY STUDIES ON THE ISOLATION OF SULFUR-OXIDIZING BACTERIA FROM SULFUR-FLOATS-SOIL COMPOSTS[1]

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The most important work on the sulfur cycle through biological processes treats the subject from two aspects. One is the study of different groups and species of organisms which are responsible for the reduction and oxidation processes in the sulfur cycle, and which have been mainly isolated from sulfur springs, canal water, sea slime, swamps, and fresh water. The other one is the study of the oxidation of sulfur in the soil.

Winogradsky (34, 35) in his classical researches described, among others, the important species *Thiothrix* and *Beggiatoa*. According to Winogradsky, the reactions involved in the sulfur transformation by thiobacteria are as follows:

$$2H_2S + O_2 = 2H_2O + S_2 + 122 \text{ calories}$$
$$S_2 + 3O_2 + 2H_2O = 2H_2SO_4 + 282 \text{ calories}$$

The H_2S is oxidized and sulfur is stored by the bacteria in the amorphous form as minute granules. The presence of sulfur in the bacteria may be demonstrated only when an excess of H_2S is present. The sulfur is then oxidized to H_2SO_4 and the process is intracellular. The sulfuric acid is neutralized by carbonates which Winogradsky supplied to the substratum.

$$H_2SO_4 + CaCO_3 = CaSO_4 + CO_2 + H_2O$$

or

$$H_2SO_4 + CaH_2(CO_3)_2 = CaSo_4 + 2\,CO_2 + 2H_2O$$

The *Thiothrix* and *Beggiatoa* were studied later by Keil (17) who confirmed the work of Winogradsky. He described the *Beggiatoa* as forming a white film, the *Thiothrix*, a grayish white film. He pointed out the autotrophic nature of the thiobacteria. Dügelli (8), in his extensive review of the work on the sulfur bacteria places the species *Thiothrix* and *Beggiatoa* as a group of H_2S oxidizing, colorless, threadlike sulfur bacteria. The *Beggiatoa* is described

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as a cylindrical threadlike cell, motile, sometimes attaining a length of 1 cm. The former is also a threadlike form, rod shaped. Both organisms are found in the slime of the sea, and in sulfur springs, but *Thiothrix* is located in the low slime, and *Beggiatoa* in the upper slime. Both of these are accompanied by infusoria, phormidium and oscilatoria. Both consume ammonia salts as a source of nitrogen and carbon dioxide as a source of carbon. Energy is derived from the oxidation of the sulfur.

Winogradsky (34) described a great many species of other sulfur bacteria which belong to the group Rhodobacter. One of the prominent species is *Thiorhodaceen;* these organisms deposit sulfur in their bodies, develop better in the light than in the dark, require less oxygen and are able to stand a higher concentration of H_2S than either the *Thiothrix* or *Beggiatoa.* They were discovered as early as 1826 by Ehrenberg of Jena, who named them *Monas Okenii.* It is reported by Jegunow (13, 14, 15) that the waters of the Black Sea near Odessa are colored red at times, because of the activities of Rhodobacter.

Another group of sulfur organisms very similar to the *Thiothrix* and *Beggiatoa* is mentioned by Düggeli. It is a group of colorless nonthreadlike H_2S oxidizing organisms. Hinze (10) described a member of this group in 1903 and named it *Thiophysa volutans.* Omeliansky (31) also described an organism of this group, *Thiospirillium Winogradskii.* Molisch (29) described *Spirilum granulatum.* The organisms of this group work slower than the *Thiothrix* and the sulfur from their bodies may be obtained as crystals from glycerin solution.

Another very important group of sulfur bacteria is the thiosulfate group. They convert thiosulfates into tetrathionate:

$$3NaS_2O_3 + 5O = 2\,Na_2SO_4 + Na_2S_4O_6$$

They were discovered by Natanssohn (30) and described in 1903. In 1904, Beijerinck (2) confirmed the findings of Natanssohn and names them *Thiobacillus thioparus.* According to the description of Beijerinck, *Thiobacillus thioparus* is a small, thin, short rod, $3 \times 0.5\mu$, non-spore forming and very motile. The organisms are kept with difficulty on solid culture media. The reaction, according to Beijerinck, is:

$$2\,Na_2S_2O_3 + O_2 = 2\,Na_2SO_4 + 2S$$

Jacobsen in 1912 (11) worked with these organisms and pointed out that even elementary sulfur is oxidized; however, while he noted the formation of sulfates he also found traces of H_2S. His best cultures oxidized only 12 per cent of the sulfur in 8 weeks. The isolations were made from sweet and sea water. Jacobsen (12) also worked with the sulfur organisms that oxidize H_2S.

Another group of sulfur organisms should be mentioned in this brief review, namely, denitrifying sulfur bacteria. Beijerinck (2) discovered them in

1904 and later in 1912 Lieske (18) studied their physiological activities. They are known as *Thiobacterium denitrificans*. They thrive in the absence of free oxygen and derive it from nitrates, liberating nitrogen. They may use either sulfur or thiosulfates. The reactions involved are as follows:

$$5S + 6KNO_3 + 2CaCO_3 = 3K_2SO_4 + 2CaSO_4 + CO_2 + 2N_2$$

or

$$5Na_2S_2O_3 + 8KNO_3 + 2NaH\,CO_3 = 6Na_2SO_4 + 4K_2SO_4 + 2CO_2 + 4N_2 + H_2O$$

The work of Gicklehorn (9) should be mentioned at this point. He claims to have studied a number of new species of sulfur organisms, some even from garden soil. His work was mostly carried out with impure cultures and only superficial morphological characters are described.

When we turn out attention to the process of sulfur oxidation in the soil, we find that very little has been done from the standpoint of microbiological elements involved. All of the studies, with few exceptions, were on the fertilizing action of sulfur. It must be kept in mind that sulfur oxidation in soils, while chiefly a biological phenomenon, may be, in part, the product of chemical reactions. This has been pointed out by Kappen and Quensell (16). However, the experiments of Boullanger (3) and Demolon (6) and Lipman and McLean (23, 24, 28) emphasized the importance of the biological factor. They proved that in sterilized soils the sulfur applied was not converted into sulfates as efficiently as in non-sterilized soils. Brioux and Guerbet (4) studied the transformation of sulfur in the soil with special reference to the oxidation of sulfur and the effect of carbohydrates, peptones and other nitrogenous materials on the process.

Lint (19, 20, 21) studied the rate of oxidation of sulfur. Shedd (32) made a comparative study of sulfur oxidation in soil and sand. Brown and Kellog (5) endeavored to determine the oxidizing power of different soils. Vermorel and Dantony (33) studied the oxidation of sulfur and iron sulfide in relation to growth of wheat and beans. Ames and Boltz (1) studied the oxidation of sulfur and its effect on availability of phosphates under anaerobic conditions and, of course, found no oxidation. This point was brought out forcibly in the work of Lipman and his co-workers. The importance of their work cannot be overemphasized. It brings the problem of sulfur oxidation to a point where both scientific and practical investigations should be followed. The work will not be reviewed here and those interested may consult the original papers.

The work reported here is an outgrowth of the investigations of Lipman. The purpose of these experiments was to study the process of sulfur oxidation, the reactions involved, the isolation of the organisms responsible for the oxidation and a study of their morphological and physiological characters.

EXPERIMENTAL PROCEDURE

A culture medium was prepared with the following composition:

	gm.
K_2HPO_4	[illegible]
$MgSO_4$	0.5
KCl	0.5
$FESO_4$	trace
$NaNO_3$	2.0
$CaCO_3$	10.0
Sugar	5.0
Sulfur	10.0
	cc.
Distilled water	1000

This medium was called medium 1. Another one, medium 2, was of the same composition without calcium carbonate. The medium was distributed into 250-cc. Erlenmeyer flasks and sterilized under pressure for twenty minutes. This method of sterilization had to be abandoned since it caused the sulfur to cake. Intermittent sterilization for ½ hour on three consecutive days was finally adopted as the best method. Six flasks of each medium were inoculated with 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 gm. of a soil-sulfur-floats compost known for its active sulfur-oxidizing power. The cultures were incubated at 25°C. Observations were made daily and after three or five days remarkable activity could be noticed in medium 1. Gas was bubbling through the medium which was ascribed to the action of sulfuric acid on the carbonate. To test the gas evolved, slight suction was applied to several flasks. Before entering the culture flasks the air was freed from CO_2 by means of concentrated potassium hydroxide solution. The CO_2 in the air withdrawn from the flasks was caught in barium hydroxide solution. The formation of barium carbonate proved that CO_2 was evolved. The degree of cloudiness served, in a way, as a measure of the activities of the organisms. The hydrogen ion concentration of both media was determined. In some flasks containing medium 2 the pH value went down to 3.0 after twelve days, while in medium 1 it was 4.8. Upon continuous transfer the activity ceased and no gas was evolved in medium 1, and in medium 2 the pH value would not go below 4.0. The original pH of media 1 and 2 were 8.2 and 6.0, respectively. Thus some oxidation must have taken place, although the lowering of the pH could be a result of the formation of organic acids from the sugar.

Plates from the same media with 1.5 per cent agar were poured and a number of bacteria and fungi were isolated. Microscopic examinations showed the presence of cocci and bacilli. The latter were different sized rods, motile and non-motile, large and very small. The representative types were inoculated on liquid medium 2. In no case did the pH value reach a point lower than 4.4 and, since some flasks with medium 2 inoculated with crude cultures gave a pH as low as 3.0 (no indicators were on hand at that time for the pH below

3.0), it was concluded that the more strongly oxidizing organisms did not appear on the plates.

The failure of the cultures to show activity upon transfer into original media showed that these media, especially medium 1, were not satisfactory. The task at hand, then, was to get a medium which would allow good growth and at the same time give an index of the growth of the organisms.

EXPERIMENT 2

Medium 3 was prepared from the following materials:

$MgCO_3$	0.5
K_2HOP_4	1.0
KCl	0.5
$FeCl_3$	trace
$NaNO_3$	2.0
Sugar (Mercks)	10.0
Sulfur	10.0
Distilled water	1000

This was inoculated in the same way as media 1 and 2. Close observations were made on the flasks and the same phenomenon as in the case of medium 1 was noticed. After 15, 25, 40, 55 and 70 and, in some series, 90 days of incubation, quantitative tests were made for the production of sulfates. The results are presented in table 1.

TABLE 1

Formation of SO_4 in cultures with different amounts of inoculum

AGE OF CULTURE	0.1 GM. INOCULUM		0.2 GM. INOCULUM		0.3 GM. INOCULUM		0.4 GM. INOCULUM		0.5 GM. INOCULUM		1.0 GM. INOCULUM	
	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.
Series 1												
days	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*
15	5.8	42.2	6.0	36.3	6.8	4.0	5.8	40.6	5.6	49.2	5.2	64.7
25	5.4	96.4	5.6	79.4	6.6	5.8	5.4	86.7	5.2	89.4	4.8	96.3
40	4.8	124.4	4.8	116.8	6.4	4.6	4.6	134.7	4.8	140.6	4.6	138.4
55	3.8	168.0	3.6	148.4	6.0	8.2	3.4	176.4	3.6	181.2	3.4	192.1
70	3.0	204.2	3.0	194.6	6.2	6.0	3.0	212.3	3.0	214.2	3.0	218.3
Series 2												
10	6.2	4.6	6.6	3.6	6.6	3.6	6.6	3.4	5.8	63.7	5.8	61.6
20	5.6	64.2	6.4	4.0	6.4	4.7	6.6	4.1	5.4	74.9	5.6	76.3
30	5.2	70.2	5.8	6.2	6.0	6.1	6.2	5.0	5.0	82.1	5.2	81.7
50	4.2	139.4	6.0	5.6	5.8	4.8	6.4	4.6	3.8	128.9	4.6	117.4
70	3.4	174.6	5.8	4.8	6.2	5.9	6.2	4.2	3.0	163.9	3.4	152.6
90	3.0	192.6	6.2	3.8	6.0	4.8	6.0	4.2	3.0	191.6	3.0	179.8

It will be noticed that the results are not uniform. In some cases no oxidation could be detected. Even those that showed maximum oxidation did not oxidize more than 8 or 9 per cent of the sulfur. Dextrose was substituted for sucrose, but with no effect. On the contrary a reduction process would go on for a while and then cease. It was ascribed then to the reducing power of the dextrose, but later it was found that even with sucrose the same thing occurred, only to a smaller degree.

The results reported in table 1 are typical of many series. In some cases even 0.5 gm. of inoculum did not give any sulfates. In the course of these two experiments numerous fungi, especially a mucor, and a fusarium accompanied the cultures. It was thought then, that the fungi participated in the early stages of the sulfur oxidation, which the bacteria continued.

Since after the second or third transfer the cultures generally deteriorated in the same way as with media 1 and 2, another set of experiments was started.

EXPERIMENT 3

It was pointed out in experiment 2, that a reducing reaction was observed when 1 per cent of dextrose or even sucrose was used in the medium. It seemed logical to conclude that in the steps involved in the production of sulfates, the reduction process is an undesirable side reaction, since in the end the H_2S formed is oxidized. Medium 3 had no sulfates to start with and, for the production of H_2S, some of the sulfur has to be oxidized first and then reduced only to be oxidized again. Therefore, the elimination of the reduction process was desirable. Since no H_2S formation was observed in experiment 1 and since the primary difference between media 1 and 3 was the carbohydrate content, a medium was prepared with 0.1 per cent dextrose and another without dextrose. It was recognized that the sulfur-oxidizing organisms in the soil may also be of autotrophic nature. In most experiments there was increased oxidation of sulfur, in medium 3 with the low dextrose content. The autotrophic nature of the sulfur oxidizing organisms in the soil was therefore tested. Cultures with medium 3 were prepared without dextrose, inoculated and incubated. The results in table 2 show that the sulfur-oxidizing organisms in the soil do not use any carbohydrate for energy and body building, but may derive their carbon needs from carbonates or CO_2 in the air, and their energy from the oxidation of the sulfur. The dextrose flasks, however, showed more oxidation than the non-dextrose. It was then ascribed fully to the stimulation of the dextrose. While this may be true it is now known from the work of Lipman, Waksman and Joffe (27), that the reaction plays an important rôle. It is therefore possible that in the dextrose flasks where fungi readily developed, the reaction favored the real sulfur oxidizers. Upon continuous transfer in the dextrose-free media activity ceased, the reaction would not go down and no oxidation would take place. On the other hand, the dextrose medium gave better results and the cultures were transferred continuously from 25-, 50-, and 90-day cultures with satisfactory results.

In many instances the cultures deteriorated but in two cultures which were freed from all the fungi except the fusarium, the oxidation of sulfur reached the 18 per cent mark. The pH was below 2.0. Attempts to continue the work with that particular culture on the same medium failed. Further modifications were necessary. The work of Lipman and McLean (23, 28)

TABLE 2

*Sulfates produced in the presence or absence of dextrose**

AGE OF CULTURE	WITH DEXTROSE				WITHOUT DEXTROSE			
	First transfer		Second transfer		First transfer		Second transfer	
	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.
Series 1								
days	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*
10	6.8	6.4	6.2	8.6	6.2	8.6	6.8	4.6
20	6.6	4.6	5.4	38.4	6.0	10.3	6.4	8.4
30	6.0	8.4	5.0	42.3	5.4	22.7	6.4	6.8
40	5.4	16.4	4.6	58.6	5.2	40.6	6.2	6.2
50	5.0	28.8	4.0	86.4	4.6	73.8	6.0	10.2
60	4.6	42.8	3.2	98.4	4.0	94.7	5.8	21.6
70	3.2	80.1	3.0	146.4	3.6	128.7	5.0	38.9
80	3.2	96.6	3.0	184.6	3.0	198.4	4.8	42.7
90	3.2	101.2	2.6	288.6	3.0	238.6	4.4	59.6
Series 2								
	WITH DEXTROSE				WITHOUT DEXTROSE			
	Second transfer		Third transfer		Original inoculation		First transfer	
10	6.8	5.8	6.4	7.9	6.0	12.4	6.0	16.4
20	6.4	7.6	5.2	40.3	5.2	43.7	5.8	18.4
30	5.8	14.9	4.8	59.6	4.8	76.4	5.0	46.9
40	4.6	60.4	4.0	94.6	4.0	101.3	4.6	70.3
50	4.2	92.4	3.0	186.1	3.4	176.4	4.4	84.6
60	4.0	116.7	2.6	270.0	3.0	242.6	4.0	112.8
85	3 6	164.8	2.2	328.4	2.6	306.9	3.6	151.7

* 0.2 gm. inoculum was used.

with sulfur-floats-soil composts showed an inhibitory effect of sodium nitrate on the oxidation of sulfur. This suggested the elimination of sodium nitrate as a source of nitrogen and ammonium chloride was substituted.

EXPERIMENT 4

In the course of the work, repeated attempts to plate out the cultures on the respective media with agar, in the early stages of incubation, gave mostly fungi with the mucor and fusarium mentioned and also some bacterial colonies.

Transfers of the bacteria from the plates into the liquid media either gave no oxidation, or in two cases only slight oxidation. In no case did the pH go down lower than 4.4.

Platings in the advanced stages gave no bacterial colonies and only the fusarium. Microscopic examinations of the old cultures showed the presence of very minute bacteria, rod-shaped with rounded ends. The organisms would not grow on solid media. Gypsum blocks, silica jelly, washed agar gave no results. At this point media 15 and 16 with ammonium chloride as a source of nitrogen instead of sodium nitrate, were prepared.

MEDIUM 15		MEDIUM 16	
	gm.		*gm.*
K_2HPO_4	0.5	K_2HPO_4	0.5
NH_4Cl	2.0	NH_4Cl	2.0
Dextrose	0.1	Dextrose	0.1
$MgCO_3$	0.25	$MgSO_4$	0.5
Sulfur	10.0	Sulfur	10.0
	drops		*drops*
$FeCl_3$, 10 per cent solution	2–3	$FeCl_3$, 10 per cent solution	2–3
	cc.		*cc.*
Distilled water	1000	Distilled water	1000

As in the early part of the work, the medium was distributed in 250-cc. Erlenmeyer flasks. Inoculations were made from the original sulfur-floats-soil composts and also from the best culture from experiment 3, where the pH was below 2.0. After several preliminary experiments medium 16 was adopted as the best. In the early stages of the cultures, the fungi would appear on plating. As in the earlier work, the mucor and fusarium predominated. Aspergilli and penicillia were also present, but on long incubation and transfer they disappeared, leaving only the minute bacteria and in some cases the fusarium. Table 3 gives the results. It will be noticed that in the third transfer, the oxidation of sulfur was very rapid after the reaction reached pH of 2.0. Attempts were made to adjust the reaction with sulfuric acid, but the work in this direction was of a preliminary nature and failed. However, later the importance of the reaction of the medium was demonstrated. An analysis of the sulfur left showed that 48 per cent had been oxidized. One cc. of the liquid required 8.3 cc. of 0.1N NaOH for neutralization. Further transfers from the 150-day culture upon other media as reported in the work of Lipman, Waksman and Joffe (27) proved the purity of the culture.

Mention was made in experiment 1 about the isolation of bacteria which brought down the reaction of the media to a pH 4.4. These organisms readily grow on the solid Czapeck's synthetic medium. They are small rods, non-motile, and showed only the Brownian movement. On Czapeck's slants they make a fairly good growth which is spreading, somewhat raised, odorless and of a slimey consistency. Two organisms were selected which did not differ

TABLE 3

Sulfates produced with NH_4Cl as a source of nitrogen

AGE OF CULTURE	ORIGINAL INOCULATION 0.2 GM. INOCULUM		FIRST TRANSFER FROM 30-DAYS-OLD CULTURE		SECOND TRANSFER FROM 25-DAYS-OLD CULTURE		THIRD TRANSFER FROM 25-DAYS-OLD CULTURE		
	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Reaction	SO_4 per 100 cc.	Titratable acidity, $\frac{N}{10}$ NaOH required to neutralize 1 cc. culture
days	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*	*pH*	*mgm.*	*cc.*
10	4.4	63.6	4.2	84.2	4.0	92.4	4.2	102.6	
15	4.2	78.9	3.8	140.6	3.8	138.6	3.6	146.7	
20	4.0	136.4	3.6	192.4	3.4	198.4	3.2	216.8	
25	3.8	151.2	3.0	246.8	3.0	238.7	3.0	242.6	
30	3.6	174.7	2.8	309.6	2.6	316.4	2.8	308.6	
40	3.0	248.6	2.6	336.4	2.4	354.6	2.4	364.5	
50	2.8	300.2	2.2	400.6	2.0	489.9	2.0	469.7	
60			2.0	584.6			1.8	689.7	
70			1.8	628.8			1.6	792.6	
80							1.4	927.3	
90							1.4	984.6	
100							1.2—*	1016.8	2.75
120							1.2—	1203.6	4.80
150							1.2—	1381.4	8.30

* No indicators were available to measure the pH below 1.2.

morphologically but did differ quite distinctly physiologically. Their laboratory numbers were cultures 5 and Z. Culture 5 had the property of liquefying gelatin. Besides these bacteria, the mucor and fusarium mentioned were also selected to try out their oxidizing power. The amount of phosphate made soluble from floats in liquid culture was taken as a measure of the oxidizing power. The medium used had the following constituents:

	gm.
[illegible]	[illegible]
$MgSO_4$	0.5
KCl	0.5
$FeSO_4$	0.01
$(NH_4)_2SO_4$	2.0
Floats	10.0
Dextrose	1.0
Sulfur	10.0
Distilled water	1000

The medium was placed in flasks and sterilized in the same manner as those used in the early part of the work. Inoculation was made from slants and incubated at 27°C. Table 4 indicates the results.

The lowering of the reaction to pH 2.6 by culture 5 looked suspicious and, although no contamination could be observed microscopically, and the bacterium was again obtained on plates with ordinary agar, it is likely that some other culture accompanied it. The results with the fungi are remarkable. The cultures were kept for over six months and the reaction did not go down any lower than pH 2.4. That they are able to oxidize sulfur could be seen from the fact that 40 per cent of the insoluble phosphates went into solution. It is possible that the process of sulfur oxidation in the soil is a result of associated activities of different forms of microörganisms. This opinion has been repeatedly expressed by Dr. Lipman, and it seems to hold true.

TABLE 4

Phosphorus made available by different microorganisms

AGE OF CULTURE	REACTION				
	Mucor	Fusarium	Culture 5	Culture Z_n	Combination of all four cultures
days	*pH*	*pH*	*pH*	*pH*	*pH*
8	6.0	6.0	6.5	6.4	4.4
18	3.2	4.4	6.2	5.8	4.4
25	3.0	3.0	3.8	6.0	4.2
50	2.6	2.6	2.6	4.2	3.0
*Phosphorus in 100 cc. of medium at the end of incubation.**					
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
	86.1	89.4	58.29	25.2	97.4

* The total amount of P in medium was 153 mgm., of which 26.4 mgm. were in solution to start with.

SUMMARY

1. The sulfur cycle from a biological standpoint has been studied from two aspects: (*a*) oxidation and reduction by sulfur bacteria from canal water, sea slime, sulfur springs, etc., and (*b*) oxidation of sulfur in soils.

2. The more important of these studies are briefly reviewed.

3. The work on the isolation and studies of the sulfur-oxidizing organisms in soils is reported.

4. The presence of a specific organism which in one hundred and fifty days oxidized close to 50 per cent of the sulfur is demonstrated and its purity apparently proven.

5. Associative action of fungi and bacteria in the oxidation of sulfur in soils is discussed.

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THE EFFECT OF DRYING SOILS ON THE WATER-SOLUBLE CONSTITUENTS[1]

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INTRODUCTION

The effect of drying and of burning soil on the growth of crops was noted in the field by the Roman farmer many years before the beginning of the science of soils. At first, improvement in the crop was attributed to the well known effect of drying on the physical condition of medium and fine-grained soils; later, as chemistry developed, the increased growth was considered to be due to some chemical change which occurred in the soil during the process of drying; while a more recent idea is that the improvement is brought about by readjustment in the microscopic life of the soil.

For several decades greenhouse growers have practiced heating the soil to kill various plant and animal enemies of the crop. In many instances the improvement in growth was greater than could have been affected by sterilization alone, the rank growth of stem and dark green color of leaf being particularly noticeable. Some growers have found it necessary to withhold a portion of the nitrogen usually supplied, to avoid excessive growth of the vegetative portion of the plant and thus permit proper fruiting.

It is the purpose of this paper to review the observed effects of drying and heating soils, and to present some experimental data indicating the effect of drying, and of heating at 105°C., on the amount of total water-soluble solids recovered by extraction with distilled water.

REVIEW OF LITERATURE

Davy (17) says:

"The improvement of lands by burning was known to the Romans. It is mentioned by Virgil in the first book of the Georgics. It is a practice still much in use in many parts of these islands; the theory of its operation has occasioned much discussion, both amongst scientific men and farmers. It rests entirely upon chemical doctrines; and I trust I shall be able to offer you satisfactory elucidations on the subject."

Also:

"When clay or tenacious soils are burnt, ... they are brought nearer to a state analogous to that of sands. . . . . All poor siliceous sands must be injured by it (burning), and here practice is found to accord with the theory."

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Warington (102) working with soils that had been dried at 55°C. for 8 hours found that the first 150 cc. of extract from 7 pounds of dry powdered soil, contained all the chlorides and 98.8 per cent of the nitrates. He states that, if the soil were wet, a much greater volume of water would be required to leach out all the chlorides and nitrates as it would be necessary to displace all the water present in the soil. He noted that oven-drying caused a reduction in quantity of nitrates, that the decrease was not so great when the soil was dried slowly and that, when air-dried at 10°C., there was an increase in nitrates.

Frank (24) extracted 30 gm. of soil with 2 liters of distilled water, comparing unheated, air-dry soil with the same heated in an autoclave at 100°C. Heating increased the total soluble matter in sand 50 per cent and in the swamp soil over 150 per cent. The soluble organic matter was almost trebled in each case. Larger crops of oats and yellow lupines were produced on the heated soils.

Liebscher (60) found that heating soil with steam increased the solubility of phosphorus and nitrogen compounds.

Schmoeger (88) heated moor soil at 150 to 160°C. for 10 hours, with the result that the phosphorus soluble in hydrochloric acid was doubled.

Deherain and Demoussy (18) heated two soils in an autoclave at 120°C. for 1 hour. When these heated soils were inoculated with fresh soil, they produced more nitrate nitrogen and ammonia than did the original soils.

Pfeiffer and Franke (73) heated soil under a pressure of 1 atmosphere for 3 hours. The soil so treated produced a larger crop of mustard than the unheated soil and it contained a higher percentage of nitrogen.

On heating a garden soil in an oven at 100°C., on 3 successive days, Richter (82) found that the amount of water-soluble organic matter trebled, and the total soluble matter almost doubled.

Tacke (100) showed that a fresh swamp soil contained very little water-soluble phosphorus, and drying at 70 to 80°C. rendered more than half of the total phosphorus soluble in water.

Tacke and Immendorf (101) found the solubility of phosphorus and potassium in some swamp soils was increased by drying at 80°C. In another experiment they found heating at 100 and 180°C. doubled and trebled, respectively, the amount of water-soluble phosphorus.

Stone and Smith (99) report that heating soil improves the color and causes an acceleration of growth of lettuce, cucumbers and tomatoes and that saprophitic fungi not found in unheated soil grew profusely on heated soil, indicating a change in the organic matter.

Krüger and Schneidewind (58) showed definitely that soluble nitrogen and phosphorus was greatly increased by heating. On both unmanured soil and that supplied with sodium nitrate, the growth of mustard was nearly doubled by heating the soil before planting.

Deitrich(19) heated garden soil and secured increased crops; but, curiously enough, pasture soils did not respond in the same way.

Whitney and Cameron (103) found that air-dried soils, in general, had more soluble phosphoric acid, nitric acid, calcium and potassium than fresh soils, and that with few exceptions oven-dried soils had still greater quantities of these materials in soluble form. Nitric acid was most variable.

Card and Blake (9) report in each of two trials, a decrease in yield of lettuce due to soil sterilization, while in one trial radishes gave an increase where nitrate of soda was added to sterilized soil.

Hassenbaümer, Coppenrath, and König (29) report that the solubility of inorganic constituents was increased when 250 gm. of soil and 3 liters of water were heated together under a pressure of 3 atmospheres for 3 hours.

King (45) reviewed fully the recorded experimental work on water extracts of soils and extraction with dilute acids. These reports date back to the work of Grouven in 1858 and include that of Wunder and Eichhorn, 1860, Peters, 1860, Jarriges, 1861–1862, Hoffman, 1863, Schulze, 1864, and Hayden, 1865. Nearly all of these investigators report potash,

lime, magnesia, soda, oxide of iron and aluminum, phosphoric, sulfuric and carbonic acids, chlorine, silica and organic matter separately. Their results vary greatly for any one constituent because of the wide range of soils, temperatures and moisture contents used.

These results are especially interesting since several of them were obtained by methods essentially similar to those of King, who used 100 gm. of soil and 500 cc. of distilled water. The soil was stirred in a mortar with enough water to make a thick paste in order to break down all granules, after which the remainder of the 500 cc. of water was added. Then the supernatant, turbid liquid was transferred to a pint Mason jar and, usually within 15 minutes, to the Pasteur-Chamberland filter chamber.

Filtration was accomplished by a pressure of 30 to 40 pounds. Clear extracts were obtained in 5 to 20 minutes, depending on the type of soil, and the amount of clay and fine silt remaining in suspension to coat the walls of the filters. It was during the 3 minutes of active agitation that the main part of actual solution occurred. It was found that longer washing did not materially increase the amount of salts going into solution. At first the electrical-resistance method was employed for determining concentration but it was found more accurate to evaporate definite quantities of the extract, dry in an oven and weigh. NO_3, HPO_4, Cl and SiO_3 were determined by methods described by Whitney and Cameron (103). Comparisons were made of the salts that could be recovered from fresh soil, soil quickly sun-dried and from that oven-dried at 110°C. Eight soils in four 1-foot sections were used. In the surface foot, of four soils the oven-dry soil had more nitrates, while in the other four, the fresh, moist soil had more; but in the second, third, and fourth sections the nitrates were increased 108, 134 and 61 per cent, respectively. In two of the eight soils the fresh sample showed considerably more HPO_4 in the first section than the dry and in eight instances in the other 3 feet out of the 24 possible cases the fresh soil was slightly higher. In every case (except one in fourth foot), the dry soil gave up much more SO_4; for the eight soils the average increase for the four sections was 265, 310, 281 and 79 per cent, respectively. In one instance only was the fresh soil significantly higher in HCO_3 while in the others the dry was from 48 to 73 per cent higher. Silica was 588, 322, 237 and 236 per cent higher in the oven-dried soil in the four sections. Chlorine was the only element that, on the average, was recovered in smaller quantity from the dry soil. The other acid radicals ran from 1.26 times as much nitrates up to 6.58 times as much of silica in the dry as in the fresh soil.

Later, determinations were made of potash, lime and magnesia in the extract of fresh and oven-dried soils. In part II, King reports good correlation between quantity of soluble salts found, especially HPO_4, and crop yields for the different soil types under investigation.

King concluded that in oven-drying the last of the moisture, for a time at a temperature near the boiling point, increases the solubility of salts and might be expected also to render the organic matter more soluble. He also concluded that when a soil dries its salts are deposited as crystals on the soil particles and salts within the granules are left on the exterior. As the soil is stirred in water, these salts go into solution readily. On the other hand, in a moist soil the solution is simply diluted by adding water and the dissolved salts are disseminated through it in part by diffusion, a slow process. The solution from the dry soil is removed from it before readsorption occurs. Thus, he explains the recovery of more soluble material from the dry than the moist soil.

Hilgard (30) considered the unusual productiveness of desert soils when properly watered, due to an abundant supply of plant nutrients rendered available by the intense heating to which these soils are subjected during the warm season. With King he believed that the soluble salts, on drying, are deposited on the surface of the particles whence they may be "readily abstracted by the first touch of the solvent water," and that soils retain salts in a condition of purely physical adsorption.

Stone and Monohan (98) noted that sterilizing loam increased the growth of soybeans 14 per cent, but that sterilizing in the same way decreased the growth of soybeans in subsoil 57.7 per cent. The subsoil pots showed poor, sickly development.

Schulze (91) noticed injurious effects from sterilization at 100 to 125°C. for 1 hour, in the early stages of growth, but later these plants became more vigorous and produced a larger crop, except peas and mustard on one soil.

Darbishire and Russell (16) heated soil at 90 to 95°C. and obtained very marked increases; the wheat yield (grain), from heated soil was 3.5 times as great as from unheated, and spinach, tomato and verbena, gave over four times the yield on the heated soil. The second crop, and even the third in one case, showed the same influence, though there was no increase in legumes. Heating to higher temperatures somewhat intensified the effect.

Koch and Lüken (55) heated a poor sandy soil in an autoclave for 2 hours under pressure of two atmospheres. This almost doubled the total soluble solids, quadrupled the soluble organic matter, but increased the soluble inorganic material only slightly. Even though heated and unheated soils were fertilized alike, the heated one produced the larger crop of oats. Injurious effects following heating were noticeable, but with crops seeded later in the season this influence was not great.

Rahn (81) made an extensive study of the effect of drying on soils. After drying at room temperature, he secured markedly increased bacterial activity, the difference being greater in heavy, rich soils, and increased growth of mustard.

Pickering (74) heated a soil at 200°C. for 2 hours, finding that 2 year-old apple trees made 63 per cent more growth, produced 48 per cent more leaves containing 52 per cent more dry matter than did similar trees in untreated soil. Heating in a moist condition increased the soluble matter, both organic and mineral, more than when heated in the dry condition. Heating soil at 100°C. in a closed vessel (75) increased total soluble matter 25 per cent in one case and 107 per cent in another, and in 11 soils an average increase from 0.052 to 0.360 per cent of soluble organic matter and from 0.111 to 0.475 per cent of total soluble matter was secured.

Gedroitz (25) found that sterilization brought about an increase in the solubility and assimilability of nutritive substances.

Russell and Hutchinson (86) report that heating soil at 98°C. increased the yield of rye 60 per cent and buckwheat 31 per cent.

Mann (64) gives a brief account of the "Rab" system of rice growing, viz., "burning a mass of branches of trees or cow dung on the land" where rice is to be seeded. He states that it is an almost universal practice on the trap and laterite soils of western India and is considered essential to rice culture there. The surface soil is heated sufficiently to change the bacterial flora, increase the soluble organic matter and improve the physical condition of the soil.

King (46) treated sand repeatedly with disulfonic acid to free it from all traces of nitric acid and organic matter, then charged it with potassium nitrate, which, after a time, was drained away. After the sand dried, 50 gm. were washed with 100 cc. of distilled water, the mass was stirred continuously for 3 minutes, the solution drained from the sand and the nitric acid determined. This was repeated until ten washings in all had been made. Table A gives the results of these determinations.

After the tenth washing the sand was treated with disulfonic acid, as is the residue in an ordinary nitrate determination, and was shown to contain 0.8 mgm. of nitrates, or nearly three times the amount recovered in the second washing, more than one-fourth as much as recovered in the first washing.

King reasoned from this that each sand grain "appropriated to itself" a film of water with potassium nitrate in solution and this film adhered to the particle so closely that in stirring after adding 100 cc. of distilled water the nitrate was given up by diffusion only and not by forming a mechanical mixture of the distilled water with the film.

Lyon and Bizzell (61) found that steaming for 2 to 4 hours under 2 atmospheres pressure increased water-soluble ammonia, organic nitrogen, nitrites and total soluble matter, but lessened the amount of nitrates. On standing 56 to 90 days after heating, there was a decrease in these soluble materials, except nitrates which remained constant. Wheat grown in

steamed soils at first showed injury, but later recovered and grew better than plants on the unsterilized soil.

Two soils heated for 2 hours at 2 atmospheres pressure and another for 4 hours (62), were extracted with 5 parts of water to 1 part of soil. Total solids and inorganic matter were increased from two to six times by this heating. All other constituents except nitrates were greatly increased by heating. No ammonia was found in any unheated soil and the concentration of nitrates was decreased by heating in every case. Wheat produced a much larger crop on the heated than on the unheated soil, and the same effect was very evident in the succeeding crop of millet, but wheat seedlings grown in a 1:1 extract made immediately after steaming, were affected unfavorably. Diluting the extract of steamed soil with distilled water, 3 to 1, improved the growth of seedlings but diluting the extract of untreated soil decreased the growth of seedlings.

The same writers (62) report that soils whose moisture content was maintained at about 25 per cent by adding distilled water, for periods of 56, 82 and 90 days after heating, steadily lost in total water-soluble material so that at the end of 90 days there was but slightly more

TABLE A[1]

Observed and computed concentration of nitrate in successive washings of sand in distilled water

NUMBER OF WASHING	WATER RETAINED IN SAND	CONCENTRATION OF SOLUTION	
		Observed	Computed
	gm.	*p. p. m.*	*p. p. m.*
1	12.7	35.750	43.4551000
2	13.2	3.300	4.8969000
3	13.1	0.451	0.5710100
4	13.4	0.174	0.0661390
5	13.05	0.138	0.0078153
6	13.3	0.128	0.0009023
7	13.5	0.110	0.0001059
8	13.5	0.110	0.0000126
9	13.5	0.110	0.0000015
10	13.4	0.110	0.0000002

than one-fourth as much soluble material present as immediately after heating. Nitrates decreased also, but in one soil they seemed to recover in part at the close of the period.

In a more extended experiment along the same line, soils stood 34 and 39 days after heating. Total solids, inorganic matter and ammonia nitrogen decreased rapidly, while there was a slight increase in nitrates in the same time.

Fletcher (23) relates that burning organic matter, twigs or manure, or both, greatly increased the yield of crops, but not to so great an extent as did heating the soil directly at 200 to 230°F.

Aitken (1) reports an instance of increased productiveness following heating of the surface garden soil by a "large and long-continued fire."

Howard and Howard (36) mention the beneficial effects, noted in parts of India, of exposing soil to the strong heat and light of the sun in April and May.

In soils kept moist for various lengths of time in open pans, Pickering (76) noted that the soluble matter, both organic and inorganic, increased as the temperature was raised from 30 to 150°C. The quantity of soluble matter decreased as the time since heating increased, up to 112 days when the last determination was made. In case of the inorganic matter at

[1] Letters used for tables derived from the literature.

100°C., however, there was an increase at both 44 and 112 days. When the soils were kept in sealed flasks there was an increase after 10 days in every case except that of inorganic matter at 125°C. When stored in sealed flasks for 43 days, the soils heated at 100 and 125°C. showed slight increase of soluble matter. When stored for 116 days there was a gain in the amount of soluble organic matter at the above temperatures but a loss in the quantity of soluble inorganic matter. Storing in light or darkness made no appreciable difference. In the case of the soil that had been heated at 125° there was no difference in organic matter whether stored at 15° or 5°, but that was a rather marked increase of inorganic matter for the lower temperature.

Pickering (77) secured increased growth of grasses and non-grasses (except in a preliminary experiment with the latter) when planted in soils previously heated. The amount of growth increased as higher temperatures were used. This increased growth correlates fairly closely with increase in soluble material, both organic and inorganic, resulting from heating.

Hall (26) says, in speaking of effect of sterilization of soil, "Approximately, the crop becomes doubled if the soil has been first heated to a temperature of 70 to 100°C. for 2 hours," while volatile antiseptics bring "about an increase of 30 per cent or more."

Russell (85) discusses briefly the beneficial effects of sterilization by heat and antiseptics, and assigns killing of the larger soil organisms which destroy the beneficial ones, as the explanation of the effect of this treatment.

Dyer (20) states that commercial vegetable growers near London partially sterilize their greenhouse soils with steam and if they use the ordinary amount of nitrogenous fertilizer the plants grow so rank as to "spoil their bearing capacity."

Seaver and Clark (92) heated soils from New York, Massachusetts and North Dakota. They found that the soluble matter in extracts of heated soils was generally six to ten times as great as that from the same soil not heated. The increase varied somewhat with the organic content of the soil, the temperature to which it was heated, and the period of heating.

Hinson and Jenkins (31) state that tobacco plants in steamed soils start quicker and grow faster than in unheated soil. They think this accelerated growth due to warming the soil, possible solvent action of the steam on the plant-food, but surely, in part, to change in the "microbe life in the soil."

In Kentucky, it is a common practice among tobacco growers to heat or burn the soil of the tobacco beds to kill weed seeds and disease.

Nagoaka (69) reports a material increase in solubility of phosphorus in dilute acids after heating the soil. He found autoclave heating had greater effect on solubility than other methods.

Peterson (72) heated wavellite and found that it increased the quantity of phosphorus soluble in 0.2 N nitric acid from 4.12 per cent of the total phosphorus, in unheated material, to 54.9 per cent in wavellite heated to 160°C., 49.0 per cent at 200°, and 98.7 per cent at 240°C. He noted little effect on soil at 100°C. but at 200°, after a five-hour treatment, there was a marked increase in solubility of phosphorus.

Ritter (83) experimented along the same lines as Rahn and found that drying increased bacterial activity, and with less effect on light than on heavy soils.

Fischer (22) comments on the work of Rahn and Ritter, but holds the chemical factor more important than the bacterial. He attaches much importance to oxidation since drying increases the amount of nitrates, even though it kills nitrifying organisms; also credits colloids and surface tension with playing important rôles.

Schreiner and Lathrop (90) in studying the chemistry of steam-heated soils made 1 to 4 extracts. Many organic compounds were found in heated soil that were not isolated from fresh soil. Dihydroxystearic acid was increased when present in the fresh soil and produced when not present. Seedlings were grown in the extracts for 10- and 15-day periods; extracts from heated soil depressed growths. Heating increased acidity.

Skalskii (94) found that sterilizing with chloroform and with heat increased the yield of crops by converting phosphoric acid and nitrogen into available forms.

Stone and associates (97) report greatly increased bacterial development in extracts from soils rich in organic matter, which had been heated previously, while it was retarded in extracts from poor soils. They consider the chemical factor most important in accounting for the effect of heating.

Leather (59) in studying the nitrate content of soils, at Pusa states that drying in the sun effected an increase as great as 400 per cent.

Seaver and Clark (93) found an increase in total soluble solids, organic matter, inorganic matter and total nitrogen, in soil when heated at 90°C. and still greater increases at 120, 150 and 170°C. Plant growth was accelerated by heating at 90 and 120°C. but retarded at the higher temperatures, which, however, increased the growth of fungi. They noted that heating increased acidity and suggest that this may account for the better growth of plants such as blueberry on "burned over" soils.

Lyon and Bizzell (63) have shown that when a soil has been heated to complete sterility by steaming and subsequently maintained at a moisture content of 25 per cent of its dry weight, the total solids decrease rapidly, as shown in table B.

TABLE B

Effect of standing on the water-soluble constituents of heated soils

	PARTS PER MILLION OF DRY SOIL		
	Total solids	Nitrates	Ammonia nitrogen
Soil 1, Dunkirk clay loam			
Freshly heated	3334	64.9	33.0
5 weeks after heating	2161	61.9	41.5
14 weeks after heating	1740	69.0	51.0
Soil 2, Volusia silt loam			
Freshly heated	3020	175.1	33.5
5 weeks after heating	2098	178.2	36.5
14 weeks after heating	1801	191.5	45.0
Soil 3, Dunkirk clay loam with extra organic matter			
Freshly heated	7194	234.0	84.1
5 weeks after heating	3288	306.0	79.5
10 weeks after heating	2719	282.5	96.0
19 week safter heating	2173	160.0	111.0

The nitrates have been affected but slightly, except in Dunkirk clay loam with extra organic matter, where there was an increase during first 5 weeks, but a rapid decline later, and, in general, an increase in ammonia nitrogen.

In another experiment, freshly heated soil had 1010 parts per million of total soluble solids and 246 parts per million of inorganic, while after 3 months the corresponding amounts are 590 parts per million of total soluble solids, and 126 parts per million of inorganic. When aerated during the 3-month period, there is a further decrease to 434 and 120 parts per million, respectively.

Russell and Petherbridge (87) state that plants grown on soils heated at 100°C., in comparison with unheated soils, have larger leaves of deeper green color and stouter stems, they flower earlier and more abundantly, the fruiting is more prolific, and they contain a higher percentage of nitrogen and sometimes phosphoric acid in their dry matter.

König, Hasenbäumer and Glenk (56) heated soil at 95°C. in a vacuum, which, in most cases contained markedly more water-soluble organic matter as well as total soluble solids

than did unheated soils. Heating at 150°C. still further increased the solubility of both organic and mineral matter. In most comparisons, heating increased the amount of water-soluble phosphorus, yet a few gave slightly less. Pot experiments with oats showed that heating in a vacuum at 95 to 98°C. increased the growth.

Wilson (106) secured slightly increased growth of plants in soil heated at 95°C., but retardation at higher temperatures, the effect varying with the kind of soil and nature of crop grown.

Buddin (8) found the nitrate content, immediately after drying in a thin layer in laboratory for 24 hours, unaffected, but reducing the moisture content further during 46 hours did increase the nitrate content slightly. When the dried soils were remoistened and incubated for 40 days, there was a marked increase in nitrates; untreated moist soil 36 parts per million, soil spread in gallery 46, and in glass-house 53.5 parts per million.

King (48) relates that the residents of northern China build flues ("Kangs") of sun-dried bricks made of "soil or subsoil mixed with short straw or chaff." After two to four years' use, these flues become defective, so that they must be replaced. When removed the bricks are finely pulverized and used as fertilizer, being planted in hills with the seed. The soil while used as a flue has become thoroughly air-dry and on the inside of the flue, undoubtedly, much of it has at times been freed of uncombined water. During this long-continued drying, the plant nutrients have been rendered more available and this fact is made use of by the Chinese farmer. King (47) suggests "absorption of the products of combustion" by the "brick" as an additional factor in giving them value as fertilizer.

Kelley and McGeorge (40) review briefly the history of burning soils. There are, in Hawaii, large areas of heavy soil which do not, when first plowed, produce satisfactory crops. It requires several months of cultivation before crops thrive. It has been noticed that on small spots where brush has been burned cotton grows exceptionally well. It is suggested that this effect may be due to heating the soil rather than to the soluble oxides of phosphorus, potassium, calcium and magnesium in the ash, since fertilizers do not produce such beneficial results.

They report results of analyses of the 1:5 water-extract of a brown ferruginous clay soil and its subsoil, and a similar type which had been plowed and was growing pineapples. Determinations were made on fresh, air-dried and oven-dried samples, extracted respectively for 1 hour, 24 hours and 7 days. Phosphoric acid (P_2O_5) was always highest in the oven-dried soil, manganese oxide (Mn_3O_4) always higher in air-dried than in fresh soil (not determined in oven-dried soil). Lime (CaO) was highest in the oven-dried soil in three of nine comparisons only. Magnesia (MgO) varied, in some samples higher in the air-dried. Sulfuric acid (SO_3) was highest in the fresh soil oftener than in either of the others, and potash was highest in the air-dried soil (with one exception) in the two surface soils, while in the subsoil the fresh soil held first place.

When all the comparable data are considered we see that in three cases the fresh soil was highest in total soluble solids, in three cases the air-dried and in the other three cases the oven-dried soil stood first. So no conclusion as to the effect of heating on total soluble salts can be drawn from these figures.

In general, extracting for 24 hours or for 7 days gave but slightly higher results than extracting for 1 hour, except in the case of phosphorus which increased in solubility with longer extraction. In two out of eight trials, heating at 100°C. increased the nitrate content; in four soils it was decreased while in the other two there was no change. As the soil was raised to higher temperatures, 150 to 200 and 250 nitrates decreased rapidly until almost none was recovered at the highest temperature.

These investigators think both chemical and physical factors enter into an explanation of the effect of drying on the soluble constituents of soils, but that "the most important set of factors affecting the solubility of inorganic soil constituents are physical in nature. Also that the physical factors act through the effect of changes in soil moisture on the physical properties of the soil." "The conditions conducive to the formation of a colloidal state and

the subsequent relation of heat to the destruction of this colloid are two of the most important of these factors." When soil contains some capillary or film water this moisture is distributed about the particles as a thin film varying in thickness with the quantity of water present in any given soil. It is stated that the moisture film in air-dry soils is held with a force equal to 10,000 atmospheres and that under such conditions "the concentration of film water with reference to the mineral matter should be much greater than that of the free or capillary water in the soil." They hold that air-dried soils should, and their results are claimed to, show least solubility.

The films with organic and inorganic matter in solution may be looked upon as colloidal in nature. Upon heating to 100°C. alteration in the film occurs through evaporation and by partial dehydration of the colloids, destroying the pressure by which the film was previously held around the particles. During evaporation the concentration of the soil moisture would increase to the saturation point, after which mineral matter would be deposited with further evaporation.

The solution obtained upon adding water to oven-dried soil should be of greater concentration than that from air-dried soil. With water films absent and the colloids altered, the water has more ready access to the soil particles. They found some mineral constituents more soluble at 250°C. than at 100°C. and think it due to "more complete elimination of soil moisture and especially the water of chemical combination."

Hulett and Allen (37) showed that the concentration of the solution in equilibrium with a curved surface is greater than that in equilibrium with a plane surface and that gypsum is most soluble in water at 40°C. Above 80°C. it is less soluble than at 0°C.

McGeorge (66) reports further results of heating soils in sunlight, in an oven for 2 hours at 80, 110 and 165°C., and in an autoclave for 1 hour at 10 pounds pressure. Onions and cowpeas showed detrimental effects while millet showed increased vigor with the higher temperature of sterilization. Heating gave better results than volatile antiseptics.

Ehrenberg (21) speaks of the old custom of using as fertilizer old garden walls made of soil and says that many soil workers have noted an improvement as the result of a soil drying out. He thinks soils rich in organic matter, only, are affected materially by drying.

Hall (27) allowed eight pots of similarly treated Dunkirk clay loam to dry from October 19 to March 1. At this time the moisture content of four pots was brought up to 20 per cent and held there until April 12. The other four continued to dry until March 19, at which time the moisture content was 1.8 per cent. The first four pots had an average of 847 parts per million (of dry soil) of total soluble solids and 5.18 parts per million of nitrates, while the average for the four air-dry soils was 1303 parts per million of total salts and 324 parts per million of nitrates, a marked increase due to drying. In October, a sample of the soil was dried. In March it had 1628 parts per million of total soluble-matter and 397 parts per million of nitrates. A sample of the original soil bottled at 12.2 per cent moisture in October had in March 1459 parts per million total salts and 495 parts per million of nitrates. This shows that nitrification had been active as in the soil which dried to March 1.

Klein (53) conducted experiments with Dunkirk clay loam (*a*) low in organic matter and (*b*) well supplied with organic matter, this being timothy sod which had been piled up and allowed to decay. Keeping soil *a* at 15, 20, 25 and 30 per cent moisture and *b* at these moisture contents with an additional sample at 40 per cent, gave an increase in growth of wheat on *a* with a decrease in moisture, and the same general relation held for *b* except that the soil with 40 per cent moisture gave practically the same yield as that with 15 per cent. There is no important difference in the yield of buckwheat following the wheat. Soil *a*, unplanted, contained more total soluble solids with the lower moisture contents, while soil *b* showed an increase in total soluble solids with an increase in the water content. Nitrates decreased with the lowering of the water content. Difference in water content had no effect on solubility of potassium, calcium and phosphorus in this soil. Air-drying reduced the nitrates, but when later brought up to and kept at optimum moisture content for various periods greater than 16 days, the nitrates increased materially. The nitrifying power and power to produce carbon dioxide is, in general, affected in the same way.

Wilson (105) found that heating at 60 to 150°C. for 2 hours increased the amount of soluble matter and changed the physical condition so that its water-holding capacity was affected. He accounts for increased productivity on these grounds.

Buck (7) reports results of a study on the effect of heat on soils, by Mann who found the water-soluble constituents increased with the rise in temperature to which the soil was heated. He notes greater growth of rice seedlings immediately after heating, quite the reverse of his experience with other plants, which may be due to the ability of the rice seedling to withstand any harmful effects of, or to use in growth, the ammonia which many hold to be a result of heating.

The work of Kelley and Thompson (41) shows that nitrates undergo decomposition, gradually disappearing as the temperature is raised. Only slight decomposition took place at 100°C. Steam heating at 2 atmospheres produced effects similar to those resulting from heating at 150°C. without pressure.

Bouyoucos (5) heated sandy loam, loam, clay and peat at 15 atmospheres pressure in an autoclave for three hours, thereby increasing the water-soluble material, as shown by the depression of the freezing point, respectively, 75, 50, 190 and 333 per cent.

In explanation of the effect of heat, he points out that water films in intimate contact with the soil particles are more concentrated than capillary or interstitial water, due to the slowness of diffusion. If only the capillary water is extracted, the quantity of soluble matter recovered would be less than the total actually in solution in the soil moisture. He suggests that adsorption may account for a higher concentration at the immediate surface of the particles than in the bulk of the solution. Furthermore, there is wide variation in the solubility of the minerals composing the soil and because of the extremely slow rate of diffusion, different mineral particles would be enveloped by films of varied concentration. This, too, would interfere with recovering from moist soil all of the soluble material.

Allen and Bonazzi (2) quote Stevens and Withers showing "only about 40 per cent of the nitrates were recovered by 1:3 extraction when small quantities were added and more than twice this amount when larger quantities were added." Allen and Bonazzi recovered in the first extraction (1:5 with 100 gm. of soil) from 65.9 to 83.9 per cent of the nitrate added, or as an average of ten results reported, 77.4 per cent.

Potter and Snyder (78) report a recovery of 93 to 97 per cent of the nitrate added at the rate of 3 parts per million of soil (phenoldisulfonic acid method).

These authors (79) report complete extraction of nitrates when 1 part of soil is shaken with 2 parts of water for 30 minutes (aluminum reduction method).

Johnson (38) reports preliminary results, showing that heating increased the solubility of minerals and the growth of plants. Heating to 250°C. produced more water-extractable substance than lower temperatures.

Skalskij (95) in studying methods of sterilization heated soil in an autoclave for 1 hour at 2.5 atmospheres. Plants in this soil grew as well as those in soil receiving complete fertilization, the number of bacteria was greater than in the untreated soil, the inoculation coming from the air. The improved fertility was due to a large increase in the soluble phosphorus, from 47 to 121 per cent, and while the soluble nitrogen content was not affected by heating, the dark green color clearly showed an increase in the available nitrogen.

Connor (15) reports a reduction in acidity as a result of heating.

Coleman, Lint and Kopeloff (14) found that the soluble solids recovered by 1:4 extraction of a moist Penn clay loam soil (25 per cent water on the dry basis) after intermittent partial sterilization at 82°C. for 1 hour on each of 5 consecutive days, was increased 46 per cent, but the amount of soluble salts was not appreciably increased after the first day's heating. The air-dry soil (4.5 per cent moisture) when similarly treated showed no increase in water-soluble solids. Sterilization by moist heat at 120°C. for 15 minutes at 15 pounds pressure increased the water-soluble solids recovered 0.0220 to 0.1805 gm., an amount 8.2 times as great as that recovered from the original soil. It should be noted also that volatile antiseptics applied as vapor in a partial vacuum, increased the water-soluble solids in air-dry soil 22 per

cent and 25 per cent in the moist soil. When the volatile antiseptics are applied with heat (82°C.) and pressure, the amount of soluble solids in moist soil is increased 25 per cent.

Christensen (10) noted that air-dry soil had its power to liberate acid from calcium acetate considerably increased as compared with that of fresh moist soil.

Koch (54) determined the effect of sterilization on the concentration of the soil solution by means of the freezing-point method. Concentration was increased more in the heavy soils. Steaming was more effective than sterilizing with formalin. Using formalin 1:50 and steaming at 10 pounds pressure increased the concentration of the soil solution more than any other method used, in fact to three times the original concentration. In Sassafras and Penn loams it was increased, respectively, 0.24 and 0.3 atmospheres. Sterilization by the so-called "commercial" methods increased the concentration of the soil solution, varying with soil and method of sterilization. Heating with steam at 10 pounds pressure for 1 hour increased the concentration of the soil solution 0.56 atmosphere in a loam soil; with a Norfolk sand the increase was but one-fourth as great.

Stewart (96) studied water extracts of thirteen soils, of two distinct types both planted and fallow, finding as did King (44) that "poor" soils yielded extracts containing solids less soluble than solids in extracts from "rich" soils.

Hartwell and Pember (28) while investigating the effect of aluminum on barley and rye, compared unheated acid soil with samples heated at 100, 260, 360, and 420°C. The lime requirement was markedly reduced by heating and the reduction increased somewhat with the temperature. The weight of green tops of rye was reduced by heating except that heating at 420°C. caused no difference in yield. The yield of green barley tops was decreased at both 100 and 260°C. but increased at both of the higher temperatures.

Potter and Snyder (80) state that "the amount of ammonia was increased by all the heat treatments, the higher temperatures to which the soils were heated giving in general greater increases;" also that dry heating at 100°C. did not materially affect nitrates, but at 10 pounds pressure in an autoclave for 9 hours, nitrates were markedly increased while a temperature of 200°C. caused an almost total disappearance of nitrates.

Johnson (39) heated soil at 250°C. The yield of tobacco was increased 571 per cent on muck, 473 per cent on Waukesha silt loam, 150 per cent on clay, 96 per cent on fine sandy loam and 62 per cent on virgin sandy loam. A single heating gave a larger yield than did heating two to eight times at 115°C. He found, also, enormous increases in concentration of the soil extract, as shown by freezing-point determinations. Heating at 250°C. caused the highest concentration.

He classifies under eight heads the published theories explaining the effect of sterilizing soils on plant growth, three of which have some bearing on the problem in hand; (*a*) "Modified organic compounds" as already mentioned from Schreiner and Lathrop (90). (*b*) "Modified inorganic soil compounds." This theory is supported by many investigations which show that an increase in inorganic plant nutrients occurs on heating soils. (*c*) "Physical theories." The author says the physical "theories are not subscribed to by any author in particular at the present time, although it was quite generally believed at one time that all the benefit derived from burning the soil was due to purely physical changes. Some of the physical factors which play a part in soil fertility are, however, coming to be regarded as very influential in conjunction with chemical factors."

Beaumont (3) showed that drying soil caused a decrease in the amount going into suspension in distilled water or 4 per cent ammonia. Oven-drying soils and then putting them under water logged conditions increased the quantity of iron compounds soluble in dilute hydrochloric acid. He states, also, that "sterilization checked the formation of this easily soluble colloidal material."

Noyes (70) while working with adsorption of different radicals by soils and decaying leaves detected no adsorption of nitrates. He holds "nitrates are completely recovered from soil in one extraction by water, and nitrates added to soil are completely recovered in addition to those present in the soil." He noted also that the lime requirement of a residual limestone soil was higher when not heated than when evaporation is carried on in the usual way.

Robinson (84) states that the lime requirement of soils, as shown by the Veitch method, is affected by (*a*) "the temperature at which evaporation is made," (*b*) continued heating after soil is dehydrated, (*c*) length of time during which treated and dried soil is in contact with water, and (*d*) the source of heat, such as steam or sand bath or hot plate.

An enormous amount of interesting work on the soluble-solid content of soils under many different conditions of cropping is reported by King (42, 43, 44, 46), King and Jeffery (49), King and Whitson (50, 51, 52) and Whitson (104).

The literature of drying, heating and sterilizing soil has been quite extensively reviewed by Lyon and Bizzell (62) and (63), Schreiner and Lathrop (90), Kelley and McGeorge (40), Klein (53), Hall (27), Kopeloff and Coleman (57), Stewart (96), Beaumont (3) and Johnson (39).

SUMMARY OF LITERATURE

1. Heating soil in various ways for its beneficial effect on crops is an ancient practice.

2. For several decades past, commercial greenhouse men have sterilized the soil used, to kill detrimental organisms, and have noted beneficial results other than from sterilization, particularly increased growth of leaves and stems.

3. Much careful experimental work on heating and drying soils has been reported, both before soil organisms were recognized, and in connection with soil-biology studies, which shows that drying and heating soil at 100°C., or higher, increases its productiveness, even though germination may be retarded and early growth depressed.

4. The literature shows that the quantity of soluble mineral and organic constituents recovered by extraction with distilled water is increased by heating. The increase bears some relationship to the temperature of heating, the maximum of soluble constituents being found at about 250°C., above which the total salts recovered decreases.

5. Investigators are not in general agreement as to the effect on nitrates of heating at 100°C. Many workers note a decrease as the temperature is further raised and almost total disappearance of nitrates at 250°C.

6. Soil workers are not a unit as to the cause of the increase in soluble material due to drying and heating. Some hold the effect of heating to be largely physical; others that it is mainly chemical, and still others lay most stress on the biological phase. Nearly all admit that the physical is usually a factor and others add colloids as a physio-chemical factor.

7. There is wide variance of opinion as to the degree to which nitrates are recovered by one or more extractions.

EXPERIMENTAL WORK

Introduction

While the literature shows that an enormous amount of work has been done on the effect of heating at a wide range of temperatures and under varied moisture contents on the amount of soluble constituents of soils, it was considered desirable to study the effect of drying at 105°C. for 8 hours, the ordinary method of driving of so-called hygroscopic moisture, on the total soluble solids that may be recovered by 1:5 extraction with distilled water.

Method of collecting soil

The surface vegetation was removed and the surface of the soil leveled. Steel tubes of 2½ inches inside diameter at the cutting edge and 2⅝ inches above it were used. A block of wood was placed on the tube which was then driven into the soil with a sledge hammer to a depth of 8 inches. The soil within the tube constituted the "tube" surface sample. Heavy paper held in place by rubber bands was immediately placed over each end of the tube to reduce evaporation and aeration.

A sample was then collected from immediately around the tube with a 1¾-inch auger to the same depth. This was immediately placed in a 2-quart Mason jar with a minimum of evaporation and aeration. This was the "auger" surface sample.

The hole was enlarged and dug out with a spade to a depth of 12 inches and the soil from 8 to 12 inches discarded. The tube was driven down from 12 to 20 inches and protected as before. This stratum 12 to 20 inches constitutes the "tube" subsurface sample. The "auger" sample was collected and sealed as before. All samples were taken to the laboratory. The paper cap at the top of the steel tubes was removed and melted paraffin poured on so as to seal it. When the paraffin had solidified, the tubes were inverted, a portion of the soil removed and the tube sealed as above. Both tubes and jars were properly labeled and placed in a refrigerator, at a temperature of 8 to 12°C. in order to keep the soil as nearly in its original condition as possible by minimizing biological activity.

All soil samples were collected and treated in this way.

General procedure

Duplicate 100-gm. samples were weighed into aluminum dishes of known weight and placed in an electric oven at a temperature of about 105°C. for 8 hours to determine the total moisture. After these had been weighed, water-free soil from another dish was added to each to make exactly 100 gm. of water-free soil for the determination of total soluble salts and nitrates.

Lyon and Bizzell (63) have shown that aerating after heating has a marked influence on the disappearance of total soluble solids. For that reason, all soils both before and after heating were kept in closed containers to reduce aeration to a minimum.

The percentage of moisture in the fresh soil was calculated on the basis of water-free soil as 100 per cent. The method of obtaining a quantity of moist soil precisely equivalent, to 100 gm. of water-free soil, was to add to 100 gm. of moist soil 1 gm. of moist soil for every per centum of moisture in it. King's (45) method was followed throughout. Five hundred cc. of distilled water was used with 100 gm. of water-free soil. The soil was placed in a mortar, sufficient water added to make a thin paste, rubbed with a pestle for 3 minutes, and the mixture transferred to a porcelain pitcher, stirred a moment, and allowed to stand 20 minutes. Soil and water were then transferred to a Pasteur-Chamberland filter and a pressure of 15 to 20 pounds applied.

In the case of moist soil containing, for example, 20 per cent water, 480 cc. of water was added, making a total of 500 cc. precisely the same as in case of the dry soil. In this way, the calculation is simplified and the comparison is more accurate than where 100 gm. of both moist and water-free soil are used and 500 cc. of water added to each. For example, if 100 gm. soil contains 20 per cent water, only 80 gm. of soil are washed, 500 cc. + 20 gm., or cc., of water from the soil, a total of 520 cc. The ratio of soil to water is 1:6.5, instead of 1:5, as with 100 gm. of dry soil to 500 cc. of water, for which our plan calls.

The first 50 cc. of the soil extract was discarded. Two 125-cc. portions from each of the duplicate soil samples, or four portions from each soil, were placed in silica dishes and reduced to dryness on a water-bath, dried in the electric oven at 105°C., cooled in a desiccator, and weighed on an analytical balance. This weight of solids represents one-fourth of what was actually dissolved in the extract from the original 100 gm. of soil.

For determining nitrates, two 50-cc. samples from each soil duplicate, four in all from each soil, were evaporated to dryness, after adding a few drops of a saturated solution of sodium carbonate, and nitrates determined colorimetrically according to Schreiner and Failyer (89).

Experiment 1

The object of this experiment is to study the effect of oven-drying on the soluble solids and nitrate content of four types of soil found in this locality and which cover a wide range of physical composition.

Samples of four soils were collected October 24, 1918, from the Station farm at Ithaca.

1. *Dunkirk silt loam*
   A. Surface, yellow, heavy silt to clay loam
   B. Subsurface, yellow silt loam

Both surface and subsurface soil contained a few small pebbles and were very low in organic matter. This soil had been growing a heavy sod of Kentucky bluegrass for the past ten years.

2. *Genesee gravelly loam*
   A. Surface, brown gravelly loam, much coarse material
   B. Subsurface, yellowish brown gravelly loam to gravel

This was a very coarse gravelly loam containing only a small percentage of sand, little more than a trace of silt and clay, and was low in organic matter. It had been growing alfalfa and some Kentucky bluegrass for several years.

3 *Dunkirk fine sandy loam*
   A. Surface, yellow fine, sandy loam
   B. Subsurface, yellow sandy loam, sand below 18 inches

The first 18 inches of this soil were very uniform in texture. The land was naturally not well supplied with organic matter, but had been manured somewhat in recent years. It had been fallowed during 1918 and was being planted to young orchard.

4. *Volusia stony loam*
   A. Surface, brown stony loam, loamy phase, not many stones in sample
   B. Subsurface, yellowish brown stony loam, more fragments of stone than in surface.

This sample was taken near the boundary between this type and Volusia silt loam as mapped by Bonsteel, Fippin and others (4). This soil has been growing mixed grasses for some time.

Table 1 gives the results of the determinations of total soluble solids and nitrates in heated and unheated soils. The figures in the last column of tables 1, 2, 3 and 6 are in each case the product of the probable error of the difference and 3.81. It is the quantity of total solids in milligrams that the dry soil must exceed the moist (or air-dry) in order that the variation may be considered significant, that is, that the odds be 30:1 in favor of the difference being due to variation in the conditions of the experiment and not to error in manipulation.

From table 1, it is readily seen that in every case the dry soil yielded more total soluble solids than did the moist soil. The amount of nitrates varies considerably. In five of the eight tube samples, denitrification had reduced the nitrates to zero, of the remaining eleven comparisons, the moist soil was slightly higher in nitrates in six, while the dry was ahead in five cases, so no conclusion as to effect on nitrates can be drawn from this experiment. It

should be stated that there was considerable variation in the period between sampling and the determination (the last one being made August 15, 1919) so that biological action may account in part for the wide variations and the frequent high probable error of the difference. Occasionally the ice was allowed to get low in the refrigerator so the temperature became high enough for good bacterial growth. There is, however, no case in which, if the nitrates are calculated as $Ca(NO_3)_2$ and deducted from the total solids, that the conclusion or its significance is altered.

Experiment 2

The purpose of this experiment was to study the effect of storage for nine weeks at 8 to 12°C. on the quantity of soluble material when the soils were kept under somewhat carefully controlled conditions of moisture content, but under different conditions of aeration. Determinations of total soluble solids were made on both moist and dry soils.

On October 23, 1919, three soils, Dunkirk silt loam (sod), Dunkirk silt loam (stony), and Dunkirk sandy loam, were collected and treated as noted above. The first and third are the same soils as were used in experiment 1 and are similar to them in every way, these samples being taken within a few feet of the others. The third soil, Dunkirk silt loam (stony), was taken from a field growing rye and vetch. It had been well manured before seeding and has received considerable fertilizer during the past few years.

Procedure

The tube samples were sealed with paraffin at once and kept in the refrigerator for a period of 68 days to determine the effect of this method of storage. The jars containing the auger samples were kept in the refrigerator also. Total soluble solids and nitrates were determined on all of the auger samples within the next 5 days, beginning on October 24.

The remainder of each of these samples was kept in the ice-box in an open jar to allow free aeration, weighed at intervals of 1 week, and distilled water added to make up for any loss by evaporation in order to detemine the effect of this method of storage for 65 days. The principal difference in the two methods of storage is in the opportunity for aeration in the auger sample in open jars, particularly since the water evaporating was compensated at intervals of one week.

The results of the determinations are stated in table 2.

These figures show that the oven-dried soil compared with the original moist soil had in the two silt loams three to five times as much soluble solids and in the sandy loam twice as much.

The Dunkirk silt loam (sod) contained very little soluble matter, either mineral or organic, and but little more than a trace of nitrates, 1.7 parts per million in the fresh moist sample. This is in close accord with determinations made on this soil collected the previous season, though both nitrates and total solids were somewhat higher then.

TABLE 1

Soluble material obtained by 1:5 water extraction

METHOD OF SAMPLING	STRATUM	MOISTURE CONTENT†	NITRATE	TOTAL SOLUBLE SALTS				MEAN	E‡	E × 3.81
				I		II				
				A	B	A	B			
Dunkirk silt loam										
		per cent	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*			
Auger.....	Surface	22.76	0.75	34.5	36.0	35.2	35.2	35.2±0.183*	0.6837	2.605
		Dry	0.61	56.0	52.2	56.0	55.2	54.8±0.6588		
Tube.....	Surface	22.01	None	50.0	48.8	49.6	49.6	49.5±0.1708	1.347	5.132
		Dry	None	74.4	75.2	68.8	69.6	72.0±1.3364		
Auger.....	Subsurface	21.53	1.48	16.8	13.6	15.2	14.4	15.0±0.3660	0.4621	1.761
		Dry	2.34	43.2	42.4	41.0	42.4	42.2±0.3173		
Tube.....	Subsurface	21.80	2.12	17.6	18.4	17.2	16.8	17.5±0.2439	0.5453	2.078
		Dry	2.09	44.8	44.0	42.4	42.4	43.4±0.4878		
Genesee gravelly loam										
Auger.....	Surface	27.87	33.52	87.2	85.6	87.2	88.8	87.2±0.3904	4.458	16.98
		Dry	36.92	242.0	233.4	222.8	220.8	231.0±4.4412		
Tube.....	Surface	28.46	None	111.2	112.8	96.0	96.0	104.0±3.9041	4.365	16.63
		Dry	None	152.8	160.0	148.4	148.4	152.4±1.9522		
Auger.....	Subsurface	13.84	2.60	20.0	18.4	19.6	20.0	19.5±0.2688	0.3321	1.265
		Dry	1.61	38.4	39.2	37.6	38.4	38.4±0.1952		
Tube.....	Subsurface	11.51	None	14.4	15.2	9.6	8.0	11.8±1.3421	1.350	5.143
		Dry	None	20.8	20.0	20.0	20.0	20.2±0.1464		

Dunkirk sandy loam											
Auger.....	Surface	17.14	18.70	56.8	56.0	56.8	58.0	56.9±0.2(			4.942
		Dry	19.38	144.8	146.0	140.4	40.0	42.8±1.2(			
Tube.....	Surface	17.37	10.81	34.0	33.6	33.6	32.8	33.5±0.1'08	0.2978	1.135	
		Dry	9.18	78.4	78.4	79.2	79.6	78.9±0.2440			
Auger.....	Subsurface	18.26	9.85	32.8	32.0	31.2	31.2	31.8±0.3172	0.7533	2.870	
		Dry	7.31	87.2	87.2	88.0	91.2	88.4±0.6832			
Tube.....	Subsurface	24.13	None	6.4	6.4	7.2	7.2	6.8±0. 952	0.2754	1.049	
		Dry	None	12.8	13.6	13.6	14.4	13.6±0. 952			
Volusia stony loam											
Auger.....	Surface	29.00	14.54	49.6	50.0	48.0	46.4	48.5±0.6345	3.092	11.78	
		Dry	13.90	140.0	140.8	152.8	152.8	146.6±3.0258			
Tube.....	Surface	27.76	1.10	11.2	12.0	13.6	13.6	12.6±0.4881	0.8397	3.199	
		Dry	0.94	107.2	106.4	108.8	110.4	108.2±0.6833			
Auger.....	Subsurface	18.93	12.1	15.2	14.4	16.0	16.8	15.6±0.3904	0.5875	2.239	
		Dry	12.5	42.4	39.2	40.8	40.4	40.7±0.4392			
Tube.....	Subsurface	19.42	None	9.6	6.4	7.2	9.6	8.4±0.5856	0.6175	2.353	
		Dry	None	35.2	34.4	33.6	34.4	34.4±0.1952			

* The probable error of the mean R was calculated by Peter's approximation formula, given by Mellor (67).

$$R = \pm 0.8453 \frac{\Sigma (+v)}{n\sqrt{n-1}}$$

R is the probable error of the arithmetical mean of all determinations; $\Sigma (+ v)$ is the sum of the deviations of every determination from the mean, their sign being disregarded; n is the number of determinations actually made.

† All moisture percentages in this paper are based on weight of soil, water-free after drying in the oven at 105°C. for eight hours.

‡ The probable error of the difference (E) is calculated by means of the formula $E = \sqrt{E_1^2 + E_2^2}$ where E_1 and E_2 represent the probable error of the means.

TABLE 2

Effect of method of storage on soluble material in soils

STRATUM	KIND OF SAMPLE	MOISTURE CONTENT	NITRATES	TOTAL SOLUBLE SATS				MEAN	E	E × 3.81
				I		II				
				A	B	A	B			
Dunkirk silt loam (sod)										
		per cent	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*			
Surface	Auger, fresh	20.50	0.17	15.2	13.6	16.0	14.4	14.8±0.3904	0.6249	2.381
		Dry	0.52	72.0	71.2	74.4	72.8	72.6±0.4880		
Surface	Auger, stored	19.42	1.54	13.0	12.0	12.8	12.0	12.4±0.2196	0.4061	1.547
		Dry	1.28	62.4	62.4	60.8	63.2	62.2±0.3416		
Surface	Tube, stored	19.93	0.24	10.4	10.4	12.0	10.4	10.8±0.2928	0.6987	2.662
		Dry	None	47.2	47.2	50.0	50.0	48.6±0.6344		
Subsurface	Auger, fresh	15.83	None	7.2	6.4	7.2	6.4	6 8±0.1952	0.3518	1.340
		Dry	None	20.0	19.2	19.2	20.8	19.8±0.2928		
Subsurface	Auger, stored	14.62	0.39	8.0	8.4	8.0	8.0	8.1±0.0976	0.2182	0.831
		Dry	0.30	28.8	28.0	29.6	28.8	28.8±0.1952		
Subsurface	Tube, stored	15.43	None	11.2	9.6	9.6	8.8	9.8±0.3416	0.4499	1.714
		Dry	None	22.4	21.6	21.6	23.2	22.2±0.2928		
Dunkirk silt loam (stony)										
Surface	Auger, fresh	21.43	7.30	40.0	39.2	38.4	40.0	39.4±0.2928	0.4499	1.714
		Dry	5.61	144.0	144.0	143.2	145.6	144.2±0.3416		
Surface	Auger, stored	20.04	10.30	44.8	46.4	46.4	46.4	46.0±0.2928	0.5278	2.011
		Dry	9.95	125.2	126.4	126.4	124.0	125.5±0.4392		

Surface	Tube, stored	19.67	1.77	40.0	39.2	39.6	39.2	39.5±0.1464	0.2440	0.930
		Dry	1.32	130.4	131.2	131.2	130.4	130.8±0.1952		
Subsurface	Auger, fresh	13.62	3.64	26.4	25.6	26.4	26.4	26.2±0.1464	0.4169	1.588
		Dry	2.61	85.6	84.0	83.2	83.2	84.0±0.3904		
Subsurface	Auger, stored	12.43	3.67	28.0	27.2	29.6	28.8	28.4±0.3904	0.6249	2.381
		Dry	3.69	81.6	78.4	80.0	79.2	79.8±0.4880		
Subsurface	Tube, stored	13.68	1.32	23.2	20.8	20.8	21.6	21.6±0.3904	0.6249	2.381
		Dry	1.33	84.8	84.8	83.2	82.4	83.8±0.4880		
Dunkirk sandy loam										
Surface	Auger, fresh	17.95	10.65	36.8	36.8	37.6	36.8	37.0±0.1464	0.6036	2.300
		Dry	8.65	86.4	85.6	82.4	84.8	84.8±0.5856		
Surface	Auger, stored	16.56	11.62	35.2	34.4	32.8	35.2	34.4±0.3904	0.6249	2.381
		Dry	11.60	68.8	67.2	70.4	69.6	69.0±0.4880		
Surface	Tube, stored	17.22	20.00	46.4	47.2	47.2	46.4	46.8±0.1952	0.2440	0.930
		Dry	17.30	75.2	76.0	75.2	75.2	75.4±0.1464		
Subsurface	Auger, fresh	14.22	1.00	11.2	10.4	11.2	10.8	10.9±0.1464	0.4629	1.764
		Dry	0.64	20.8	20.8	18.4	20.8	20.2±0.4392		
Subsurface	Auger, stored	12.76	0.79	9.2	10.4	9.6	9.6	9.7±0.1708	0.3389	1.291
		Dry	0.62	16.8	16.8	18.4	17.6	17.4±0.2928		
Subsurface	Tube, stored	13.45	0.33	10.0	10.0	9.6	8.8	9.6±0.1952	0.2440	0.930
		Dry	0.26	19.2	18.4	19.2	19.2	19.0±0.1464		

Close scrutiny of this table reveals that in three cases the stored auger sample is higher in total soluble solids and in three cases, lower than the fresh sample. Determinations made on fresh auger samples and on the stored sealed-tube samples, therefore, are comparable.

In each soil there is evidence of nitrification in the open-jar-auger sample, the increases in the three soils being in order from 1.7 to 15.4 parts per million from 73 to 103 and from 106 to 116. In some cases the nitrates run higher in the sealed-tube soil and in some lower than in the fresh soil, so from these meagre data no conclusion can be drawn as to the effect on nitrates of storing in sealed tubes for a period of 68 days.

It appears that the effect of storing at a temperature of 8 to 12°C. in open jars for 68 days with the restoration of moisture evaporated at intervals of a week or in sealed tubes for 65 days does not materially affect the quantity of total soluble solids as determined by 1:5 extraction with distilled water, all of the soils being in the moist state. Storing decreased the soluble solids as determined in the water-free condition in five of the six comparisons made, the losses, however, were not great.

Experiment 3

The object of this experiment was to study the effect on soluble solids and nitrates of sun-, air- and oven-drying on soils that had been water-logged for a considerable period, if, indeed, ever dry since their formation.

In July, 1919, samples of a drab silt loam were collected near Cayuga Lake close to the west wall of the valley at the mouth of a small tributary. The surface and subsurface were taken with a steel tube, described above. The subsoil, 20 to 40 inches, was taken with an auger in the bottom of holes left by the tube after taking subsurface stratum. The soil suffered little, if any, change due to aeration and since it was very wet, containing 73 to 108 per cent of moisture, and the glass containers were sealed as soon as possible and placed in the ice-box on reaching the laboratory.

Determinations were made the same as in experiment 1 during the next few days on the wet and corresponding oven-dry samples and in the same way on the sun-dried samples on August 8.

Another set of samples was collected on October 16, 1919, south of Ithaca, near the east wall of the valley at the mouth of a small stream. This soil, also a drab silt loam, was not so wet as the other and contained nitrates in the subsurface, whereas the other soil had none in the subsurface.

In every case the wet soil was mixed thoroughly by hand and the total moisture determined in triplicate instead of in duplicate, as with all other soils.

The "wet" samples were oven-dried during the night and determinations made the following day, October 17. Half of the soil was set out to dry in the laboratory, as there is usually not much sunshine and rainfall is frequent here at this season. Determinations were made as soon as the soil was entirely air-dry.

The results are given in table 3.

TABLE 3

Effect of drying on soluble material in swamp soils (drab silt loam)

CONDITION	STRATUM	MOISTURE CONTENT	NITRATES	TOTAL SALTS RECOVERED				MEAN	E	E × 3 81
				I		II				
				A	B	A	B			
Inlet Valley, near Cayuga Lake and west valley wall										
		per cent	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*			
Wet as it came from field	Surface	73.67	3.66	101.6	102.4	97.6	96.8	99.6±1.1712	1.207	4.599
		Dry	3.06	161.6	160.0	161.6	160.8	161.0±0.2928		
	Subsurface	83.65	None	91.2	88.0	82.0	83.2	86.1±1.7081	2.071	7.814
		Dry	None	137.6	136.8	140.8	143.2	139.6±1.1712		
	Subsoil	107.85	None	63.2	64.0	64.8	62.8	63.7±0.3416	2.7542	10.492
		Dry	None	199.2	200.0	185.6	191.2	194.0±2.7328		
Air dried in the sun	Surface	1.88	4.60	122.4	121.6	121.6	124.0	122.4±0.3904	1.6093	6.131
		Dry	4.60	185.6	177.6	181.6	186.4	182.8±1.5616		
	Subsurface	3.13	None	152.8	148.8	148.8	148.8	149.8±0.7321	0.9349	3.562
		Dry	None	236.8	238.4	240.0	239.2	238.6±0.4880		
	Subsoil	2.89	None	123.2	121.6	122.4	120.8	122.0±0.3904	0.5187	1.976
		Dry	None	248.8	249.6	251.2	249.6	249.8±0.3416		
Inlet Valley, south of Ithaca, near east valley wall										
Wet	Surface	68.01	4.73	80 0	71.0	73.0	73.0	74.2±1.3908	2.630	10.01
		Dry	4.61	203.8	205.2	195.0	195.7	199.9±2.2322		
	Subsurface	47.83	2.11	25.0	23.0	21.0	21.0	22.5±0.7322	0.8079	3.078
		Dry	2.02	116.8	115.2	114.4	115.2	115.4±0.3416		
Air-dried, laboratory	Surface	2.42	9.45	111.2	111.2	110.4	112.0	111.2±0.1952	0.5255	2.002
		Dry	8.00	239.2	237.6	240.0	240.8	239.4±0.4880		
	Subsurface	2.20	3.34	57.6	55.2	55.2	56.8	56.2±0.4880	0.6901	2.629
		Dry	3.16	143.2	144.0	140.8	143.2	142.8±0.4880		

It will be noted that oven-drying materially increased the total soluble solids in all of the wet samples, air-drying brought about a marked increase and oven-drying the air-dry soil still further increased the total soluble solids, as shown in table 4.

In the first two columns of percentages, the increase is based on the total soluble solids in wet soil but in the third, the percentage increase is based on the total soluble solids in the air-dry soil. This increase calculated on the same basis as the first two is, for the respective samples, 83, 177, 290, 223 and 534 per cent. The increase due to air-drying before oven-drying cannot be due to any nitrification during the slow drying at ordinary temperature, as the increase in nitrates was exceedingly slight, wholly insufficient, calculated as $Ca(NO_3)_2$ to account for the change.

The marked effect of air-drying on these swamp soils may help to account for the relatively high productivity of such soils after a few seasons of cultivation, as against their low productivity when newly turned by the plow.

TABLE 4

Increase in total soluble salts due to drying

SOIL	STRATUM	INCREASE DUE TO OVEN-DRYING WET SOIL	INCREASE DUE TO AIR-DRYING WET SOIL	INCREASE DUE TO OVEN-DRYING AIR-DRY SOIL
		per cent	*per cent*	*per cent*
Drab silt loam near lake	Surface, 0 to 8 inches	60	23	50
	Subsurface, 12 to 20 inches	62	74	59
	Subsoil, 20 to 40 inches	200	94	104
Drab silt loam south of Ithaca	Surface, 0 to 8 inches	167	50	116
	Subsoil, 12 to 20 inches	412	150	154

Kelley and McGeorge (40) state:

> The solubility of soils used in aquatic agriculture is abnormally high, but upon drying out these become much less soluble and approach a state similar to that existing in aerated soils. When such soils are heated after drying, they seem to undergo changes of the same order as are produced in dry-land (ordinary cultivated) soils.

The work here reported, either experiment 3 or 4, is not in accord with their conclusions, as these soils when air-dried, had, in every case, more soluble salts than the same soils when wet.

Experiment 4

The object of this experiment was to study the effects of oven-drying on a wide range of fine-grained soils containing varied amounts of organic matter at three moisture-contents, viz., air-dry, optimum, and water-logged, with the soil kept in the latter two conditions for a period of 9 weeks.

Six soils were used, ranging in texture from clay to sandy loam:

1. *Drab*,[3] or (*Sharkey*,[4]) *clay*. This is a drab colored clay soil, not well supplied with organic matter, stiff and more or less impervious to water, very difficult to work as it is exceedingly tenacious when wet and cloddy when dry. It occurs in large areas in the poorly drained portions of the Mississippi bottom lands, especially south of St. Louis. It is more fully described by Hopkins, Mosier and associates (34), Marbut and associates (65), and as Yazoo clay by Coffey and others (11).

2. *Black clay loam*[5] (Marshall black clay loam). This is a black clay loam soil, well supplied with organic matter. It occurs in flat, depressed areas, former ponds or lakes, and is very productive when thoroughly drained. It is described more fully by Hopkins, Mosier, et al. (33), Marbut (65) and as Miami black clay loam by Coffey, Mosier et al. (12).

3. *Brown silt loam* (Marshall silt loam). This is a brown silt loam soil of good open texture, well supplied with organic matter, and very productive, occupying the rolling prairies of Illinois, Indiana and Iowa. Described by Hopkins, Mosier et al. (35), Marbut (65) and Coffey et al. (13).

TABLE 5

Organic matter contained in these soils*

SOIL	ORGANIC CARBON	TOTAL ORGANIC MATTER	MOISTURE EQUIVALENT
	per cent	*per cent*	*per cent*
1. Drab clay	2.07	3.57	41.6
2. Black clay loam	3.19	5.5	32.4
3. Brown silt loam	2.78	4.8	28.0
4. Yellow-gray silt loam	1.67	2.9	20.7
5. White silt loam	0.435	0.75	
6. Dunkirk fine sandy loam	1.856†	3.20	

* Figures on soils 1 to 4 furnished by Professor J. G. Mosier.

† This determination was kindly made by Dr. F. A. Carlson.

4. *Yellow-gray silt loam* (Knox silt loam). This is a light colored, rolling timber soil, not well supplied with organic matter. More fully described by Hopkins, Mosier et al. (33), Marbut (65) and as Miami silt loam by Coffey, Mosier and others (13).

5. *White silt loam*. This soil was not recognized as a separate type by the Bureau of Soils, as its work in Illinois was done during the beginning of American soil surveying. It is a very light gray silt loam, underlaid by a decidedly impervious stratum, known as "tight clay." It is an unproductive virgin timber soil, very low in organic matter, in fact almost nitrogen free, having but 0.7 per cent of organic matter. This soil is more fully described by Hopkins, Mosier et al. (32).

6. *Sandy loam*. This is the same soil that was used in experiments 1 and 2.

Soils 1 to 5, inclusive, are surface soils, 7 to 8 inches deep. Soils 1 to 4 have been stored in the air-dry state for two or more years in an attic where the humidity is very low and the temperature at times in summer, rather high. Table 5 gives the content of organic matter in these soils.

[3] Name used by Illinois Agricultural Experiment Station.

[4] Name used by United States Bureau of Soils, in Bul. 96, p. 738.

[5] Soils 1 to 5, inclusive, were collected by the writer while a member of the staff of the Agronomy Department, College of Agriculture, University of Illinois.

Organic carbon was determined by the Parr bomb-calorimeter method, CO_2 was measured and reduced to standard P and T from which C was calculated. $C \times 1.724$ (Wolff factor) gives organic matter. This is not claimed to be absolutely accurate nor strictly comparable since the carbon content of soil organic matter varies with its age and the conditions under which decomposition has occurred. The organic matter in white silt loam, for example, is probably more highly carbonized than that in brown silt loam and that in drab clay, a swamp soil, has been affected by a different type of decomposition from brown silt loam, a well-drained type. However, the figure for organic matter is of value in a comparative way when, as in these soils, the differences between them are marked.

Procedure

The soils were air-dried, worked over with a rolling pin, passed through a 2-mm. screen, thoroughly mixed and divided into three portions, *a*, *b*, and *c*. On samples of *a* the usual determinations of total soluble solids and nitrates were made in the original air-dry and in the water-free condition. To *b* distilled water was added, and worked by hand, until it reached what might be termed "optimum" moisture content when the soil was placed in 2-liter earthenware jars. These were weighed on a solution scale the next day and at the end of each succeeding 7-day period, when distilled water was added to restore that lost by evaporation. To *c*, in similar jars, distilled water was added to a point of saturation and more water was poured on as needed to keep the soil submerged. Then *b* and *c* were kept in the laboratory for nine weeks, except the Dunkirk sandy loam which was kept only 8 weeks. The regular determinations were made on both moist and water-free samples at the end of this time.

Results are given in table 6.

Table 6 has several outstanding features. The increase in total solids extracted from soils 1, 2 and 3, well supplied with organic matter, when the original air-dry soil is dried in the oven at 105°C. is very marked; in soils 4, 5 and 6, low in organic matter, the actual increase due to drying is less, but the amount of soluble solids varies from nearly twice to almost three times as much as that in the air-dry soil. In all, except white silt loam, which is very low in organic matter, the moist *b* samples kept 9 weeks at optimum moisture-content had a higher quantity of soluble material than did the air-dry soil, and the dry *b* soil exceeded that water-freed directly from the original air-dry condition. This increase may be accounted for by the increase in nitrates, calculated as $Ca(NO_3)_2$.

The saturated *c* samples in the wet condition showed more total soluble salts than either of the others, even though the nitrates had disappeared. When oven-dried, this soil showed the highest soluble salt content in five of the six soils, and the sixth was but 0.8 mgm. below the next higher soil, the water-freed, moist Dunkirk sandy loam. This may be accounted for in part by the very large amount of water in these soils shown in table 6 to be 75.7 per cent in drab clay down to 37.8 per cent in Dunkirk sandy loam. Here the soil solution is much more dilute and more solids tend to dissolve, as the

solution is probably far from saturated with respect to any of the salts. This soil solution upon adding distilled water to make up the total 500 cc. becomes a part of the 500 cc. and the final result is a more concentrated solution as shown by table 6. When the saturated soil was placed in the oven, water stood on its surface, so the oven-drying process required more than the usual 8 hours. This, it has been suggested, brings more organic matter and much iron and alumina into solution.

Experiment 5. Determination of hygroscopic coefficient

In the hope of securing information which might shed a bit of light on the cause of the increase in soluble material in soils due to heating, two small pieces of experimental work were undertaken, viz. (experiment 5), the determination of the hygroscopic capacity, or coefficient, of the soils used in experiment 4 and (experiment 6) a study of the retention of potassium nitrate by different grades of sand.

The soils are those used in experiment 4 which range from clay to sandy loam.

Procedure

In order to have the soils as uniform as possible, they were passed through a 1-mm. sieve. Duplicate samples of air-dry soil equivalent to approximately 2 gm of water-free soil were weighed directly into weighing bottles, 7 cm. in diameter. The soil was spread out in a uniformly thin layer over the bottom and exposed to a saturated atmosphere in a humidifier,[6] Strips of filter paper were used as wicks, increasing the surface of contact between air and water in order to insure complete saturation of the air. By means of a water-pump the air pressure within the humidifiers was reduced by several centimeters in order to hasten saturation and reduce condensation. To avoid marked sudden changes in temperature, the humidifiers were placed in a thick-walled wooden box lined with asbestos. This was first located in a cold room and heated electrically, a thermostat being used for maintaining a constant temperature. It was found after 6 weeks' work, however, that the external temperature of winter varied so much that the thermostat and heating apparatus were incapable of maintaining a sufficiently constant temperature. In several instances there was a sudden drop in outdoor temperature the day before weighings were to be made. This brought about condensation in the soil, giving hygroscopic coefficients too high and far from uniform.

The next step was to place the entire apparatus in a deep, unheated basement room. Here the temperature to which the soils were subjected remained fairly constant. The maximum variation in room temperature during the first week was from 61 to 64°F., and inside of the box from 15.5 to 17°C.; the second week the corresponding temperatures were 60.5 to 65.5°F. for the room and from 15 to 18°C. inside the box. There did not appear to be any condensation and yet there is not an altogether satisfactory agreement of duplicate determinations made the first week on soils 4, 5 and 6.

The soils were kept in the saturated atmosphere for a period of 7 days when the humidifiers were removed from the constant-temperature box. Before removing the lid of humidifiers, the pressure was equalized by admitting air *very slowly* through the side tube. Upon removing the weighing bottles from the humidifier, the lids were immediately and tightly inserted

[6] The humidifier was a large desiccator whose dehydrating substance had been replaced by a 10 per cent solution of sulfuric acid to furnish the water vapor. The desiccators are supplied with side tube and stop cock.

Effect of moisture content on soluble material in soils

CONDITION	MOISTURE CONTENT	NITRATES	TOTAL SALTS RECOVERED				MEAN	E	E × 3.81
			I		II				
			A	B	A	B			
Drab clay									
	per cent	*mgm.*	*mgm*	*mgm.*	*mgm.*	*mgm.*			
Air dry	5.59	4.00	68.0	68.0	67.2	68.8	68.0±0.1952	0.8998	3.428
	Dry	5.00	150.4	145.6	150.4	148.0	148.6±0.8784		
Optimum moisture	25.98	36.20	82.4	82.4	81.6	80.8	81.8±0.2928	0.3171	1.208
	Dry	30.60	162.4	163.2	163.0	163.2	163.0±0.1220		
Saturated	75.75	None	131.2	130.4	128.8	128.0	129.6±0.5856	0.6343	2.417
	Dry	None	168.0	167.2	166.4	166.8	167.1±0.2440		
Black clay loam									
Air-dry	5.15	2.52	72.8	72.8	71.2	70.4	71.8±0.4880	0.9001	3.429
	Dry	3.88	165.6	167.2	169.6	169.6	168.0±0.7564		
Optimum moisture	20.82	22.30	76.8	76.0	75.2	76.8	76.2±0.2928	0.3812	1.452
	Dry	17.81	183.2	184.8	184.0	184.4	184.1±0.2440		
Saturated	69.88	None	95.2	96.0	96.0	96.8	96.0±0.1952	0.8998	3.428
	Dry	None	200.0	198.4	195.2	196 0	197.4±0.8784		
Brown silt loam									
Air-dry	2.33	6.25	82.4	83.2	83.2	81.6	82.6±0.2928	0.9259	3.528
	Dry	5.54	180.8	181.6	176.0	179.2	179.4±0.8784		
Optimum moisture	21.80	44.18	98.0	98.4	97.6	96.0	97.5±0.3661	0.9178	3.497
	Dry	43.54	200.0	204.4	199.2	200.0	200.9±0.8541		
Saturated	48.74	None	115.2	118.0	116.8	115.2	116.3±0.5368	1.1996	4.570
	Dry	None	203.2	204.0	198.4	200.0	201.4±1.0736		

Yellow gray silt loam									
Air-dry	1.24	4.86	53.6	53.6	52.0	52.8	53.0±0.2928	0.4141	1.578
	Dry	4.44	96.8	95.2	95.2	96.0	95.8±0.2928		
Optimum moisture	16.85	32.32	71.2	70.4	69.6	72.0	70.8±0.3904	0.6637	2.539
	Dry	28.50	116.8	114.8	114.4	116.8	115.7±0.5368		
Saturated	44.67	None	73.6	72.8	72.8	71.2	72.6±0.3416	0.5956	2.269
	Dry	None	123.2	122.4	124.0	120.8	122.6±0.4880		
White silt loam									
Air-dry	1.25	Faint trace	34.4	34.8	33.6	35.2	34.5±0.2440	0.4603	1.754
	Dry	None	93.6	92.0	95.2	93.6	93.6±0.3904		
Optimum moisture	18.16	0.8	26.4	26.4	26.4	24.8	26.0±0.2928	0.4499	1.714
	Dry	0.2	94.4	93.6	95.2	95.6	94.7±0.3416		
Saturated	39.88	None	73.6	73.6	75.2	72.8	73.8±0.3416	0.4831	1.840
	Dry	None	100.0	101.6	100.0	99.2	100.2±0.3416		
Dunkirk sandy loam									
Air-dry	0.90	22.70	68.0	66.4	66.4	66.4	66.8±0.2928	0.8339	3.177
	Dry	18.76	120.8	122.4	124.8	124.8	123.2±0.7808		
Optimum moisture	12.41	37.58	77.6	76.8	76.8	78.4	77.4±0.2928	1.0658	4.061
	Dry	28.50	132.8	132.0	126.4	131.2	130.8±1.0248		
Saturated	37.80	None	48.8	50.4	48.8	49.6	49.4±0.2928	0.4880	2.629
	Dry	None	129.6	128.8	130.4	131.2	130.0±0.3904		

to prevent evaporation and the bottles with soil weighed at once after wiping them perfectly dry. After weighing, the soil was dried in the bottles at 105°C. for 8 hours and again weighed. The loss is the hygroscopic moisture or, expressed as per cent on the basis of oven-dry soil, the hygroscopic coefficient.

The results of the determinations appear in table 7.

As pointed out by Beaumont (3, page 492–493), the probable error of determinations of hygroscopic coefficient is high. The accuracy of this statement is well borne out by the figures in table 7. His results indicated that slight variations in temperature made little difference in adsorption of water vapor so the only effort in this work was to keep the temperature sufficiently constant to prevent condensation of free water on the particles, or in the inter-

TABLE 7

Hygroscopic coefficients of air-dry soils used in experiment 4

SOIL	WATER ABSORBED IN 7 DAYS				MEAN	HYGROSCOPIC MOISTURE	ORGANIC MATTER	TOTAL SOLUBLE SALTS AT OPTIMUM MOISTURE*	AVERAGE SOLUBLE-SALT CONTENT OF AIR-DRY OPTIMUM-MOISTURE, AND WATER-FREE SOILS*
	First trial		Second trial						
	A	B	A	B					
						per cent of dry soil	*per cent*	*mgm.*	*mgm.*
1. Drab clay...	11.66	11.62	11.30	11.62	11.550±0.061	5.59	3.57	81.8	115.4
2. Black clay loam.....	9.95	10.24	9.94	10.02	10.037±0 493	5.15	5.50	76.2	125.0
3. Brown silt loam.....	4.45	4.62	4.41	4.47	4.487±0.0322	2.33	4 80	97.5	140.1
4. Yellow gray silt loam ..	2.05	2.50	2.30	2.26	2.277±0.0598	1.24	2.90	70.8	83.8
5. White silt loam.....	1.55	1.95	1.85	1.83	1.795±0.0299	1.25	0.75	26.0	62.2
6. Dunkirk fine sandy loam	1.95	2.44	2.22	2.48	2.272±0.0915	0.90	3.20	77.4	99.5

* Data taken from table 6.

stices of the soil. This latter seems to have occurred during the early part of this work as the hygroscopic coefficient was high and quite erratic. These figures seem to bear out Beaumont's conclusion, also, that other factors than total surface affect the adsorption of water. Soils 4 and 5 are very similar in texture, consequently in total surface, and the hygroscopic moisture actually in the soils, air-dry, is the same, yet when exposed to the same saturated atmosphere, soil 4, with higher organic-matter and soluble-salt content, adsorbs 0.482 per cent more actual moisture, 27 per cent excess over soil 5, the one of lower salt- and organic-content. In this connection, let us compare soils 5 and 6, in table 7. White silt loam has much more surface than Dunkirk fine sandy loam.[7] In the air-dry state they appear in their right order as

[7] No mechanical analysis available.

regards hygroscopic moisture and surface having, respectively, 1.25 and 0.90 per cent hygroscopic moisture. However, when exposed to a saturated atmosphere for 7 days, they stand in a different relationship to each other, their positions being reversed, and instead of the soil with greater surface absorbing more moisture, more is taken up by the soil which has less surface, but contains more soluble salts. This tends to show that within certain limits, at least, soluble salts are of sufficient importance to reverse the normal effect of total surface exposed by a soil.

Considering table 7 in a broad, general way, the hygroscopic moisture content in the air-dry soil bears a normal relationship to the total surface, and when we consider surface and organic-matter content this same general relationship holds for hygroscopic coefficient except in case of the sandy loam where the discrepancy is due to its large quantity of soluble salts. The difficulty here lies in that we have not a single variable factor, but several, viz., size of particles, total surface, organic matter, and soluble salts.

Since it is almost, if not wholly impossible to control all factors at once, it may be necessary to work with synthetic soils, varying but a single factor at a time. These determinations of hygroscopic coefficients cannot yield much valuable evidence, except that, in a general way, the soils with the highest percentage of clay and colloids have the highest hygroscopic coefficients and within the limits of this experiment have the highest soluble salt content. However, the data are so meagre that no definite safe conclusion may be drawn.

Experiment 6. Retention of nitrate by quartz and white silt loam

The purpose of this experiment was to study the question whether clean quartz sand holds potassium nitrate, and if so, to what extent. This salt was selected because the acid radical is not generally supposed to be adsorbed to an appreciable degree, and also because it was available as a chemically pure substance.

The material used was a clean ground quartz. It was first leached with a 10 per cent solution of hydrochloric acid to remove any possible soluble material, then washed free of the acid and air-dried. It was then sifted into four grades, as used by the United States Bureau of Soils:

	Diameter mm.
Coarse sand	1.00–0.50
Medium sand	0.50–0.25
Fine sand	0.25–0.10
Very fine sand	0.10–0.05

White silt loam from experiments 4 and 5 was used also, since in the air-dry condition it was essentially devoid of nitrates.

The water-holding capacity of 50 gm. of each of these materials was then determined experimentally. Water was added from a burette and the materials were found to hold, without any loss by percolation on standing, the

following quantities: coarse sand, 10 cc.; medium sand, 10 cc.; fine sand, 15 cc.; very fine sand, 17 cc.; white silt loam, 18 cc.

According to Mosier and Gustafson (68) the surface per gram of the different grades, assuming perfect spheres of average diameter for the grades, is as follows: coarse sand, 30.2 sq. cm.; medium sand, 60.4 sq. cm.; fine sand, 129.3 sq. cm.; very fine sand, 302.1 sq. cm.; white silt loam, 2270.7 sq. cm. Analysis[8] of this latter soil shows (Bureau of Soils sizes) 1.5 per cent medium sand and coarser grades, 1.7 per cent fine sand, 7.5 per cent very fine sand, 70.6 per cent silt, and 18.3 per cent clay. The calculation of the surface per gram of white silt loam was based upon these percentages, the surface areas given above, and the assumption that 824.8 sq. cm. is the surface of 1 gm. of silt and that 9090.2 sq. cm. is the surface of 1 gm. of clay.

The figures for total surface per gram are undoubtedly more nearly accurate for white silt loam than for the quartz since the latter is angular and of all conceivable shapes with no spheres. The surface of the quartz must be considerably greater than the figures show, whereas in the white silt loam soil the angles have been worn off the particles to some extent, bringing them somewhat toward the spherical shape—yet the figures at best are but an approximation which may be of some value for purposes of discussion.

Solutions of potassium nitrate were then made up of such strength that 1 cc. of the first solution contained 0.1 mgm. of nitrate and the other, 0.5 mgm. of nitrate. The hygroscopic capacity of quartz is so low that this factor was ignored. A quantity of potassium nitrate solution equal to the water-holding capacity was added from an accurate burette to each of four 50-gm. samples of the grades of quartz and of white silt loam. These moistened samples were covered to prevent evaporation and set aside over night to permit of any reaction or adjustment in the moist mass, after which two samples of each were placed in the oven at 105°C. for 8 hours. Nitrates were determined immediately on the other two samples. Each was placed in a 500-cc. beaker and distilled water added to make a total of 250 cc.; for example, to the coarse sand containing 10 cc. of KNO_3 solution, 240 cc. of distilled water was added and to the very fine sand having 17 cc. of the solution, 233 cc. of water was added. Thus the relationship throughout was 1 part of soil or quartz to 5 of water.

This experiment was run in two parts, 6a and 6b. In the first part, the nitrate solution used contained 100 parts per million, or 0.1 mgm. per cubic centimeter of nitrate and in the second, the solution contained 500 parts per million or 0.5 mgm. per cubic centimeter. In all other respects the two trials were identical. The stronger solution was used in the second trial because a dilution of 10 cc. of the first solution to 250 cc. was considered too great for securing results of the degree of accuracy desired.

The results of the first set of determinations are given in table 8.

The results of the second set of determinations are given in table 9.

[8] This analysis was kindly furnished by Dr. Bizzell and Dr. Buckman.

TABLE 8

Nitrate recovered from ground quartz and white silt loam

(Nitrate solution, 100 p. p. m. or 0.1 mgm. per cc.)

SIZE OF MATERIAL	CONDITION	AMOUNT NITRATE ADDED	FIRST EXTRACTION		SECOND EXTRACTION		THIRD EXTRACTION		RECOVERED BY FIRST EXTRACTION
			NO_3 found	NO_3 in 250 cc.	NO_3 found	NO_3 in 250 cc.	NO_3 found	NO_3 in 250 cc.	
		mgm.	*p. p. m.**	*mgm.**	*p. p. m.**	*mgm.*	*p. p. m.**	*mgm.*	*per cent*
Coarse sand....	Moist	1.0	3.22	0.805	0.48	0.12	0.33	0.08	80.50
	Dry	1.0	3.15	0.79	Trace	Trace	0.36	0.09	79.00
Medium sand...	Moist	1.0	3.17	0.79	0.56	0.14	0.32	0.08	79.00
	Dry	1.0	2.82	0 705	Trace	Trace	0.32	0.08	70.50
Fine sand.....	Moist	1.5	4.67	1.17	1.03	0.26	0.42	0.10	78.00
	Dry	1.5	4.11	1.03	0.62	0.15	Trace	Trace	68.67
Very fine sand..	Moist	1.7	4.59	1.15	0.96	0 24	Trace	Trace	67.64
	Dry	1.7	4.41	1.10	0.71	0.18	0.25	0.06	64.70
White silt loam..	Moist	1.8	5.57†	1.393					77.40

* Average of four determinations.

† Average of eight determinations.

TABLE 9

Nitrate recovered from ground quartz

(Nitrate solution, 500 p. p. m. or 0.5 mgm. per cc.)

SIZE OF MATERIAL	CONDITION	AMOUNT OF NITRATE ADDED	FIRST EXTRACTION			SECOND EXTRACTION			TOTAL NO_3 RECOVERED
			NO_3 found	NO_3 in 250 cc. if homogeneous		NO_3 found	NO_3 in 250 cc. if homogeneous		
		mgm.	*p. p. m.**	*mgm.*	*per cent*	*p. p. m.**	*mgm.*	*per cent*	*per cent*
Coarse sand....	Moist	5.0	17.74	4.435	88.7	1.21	0.302	6.0	94.7
	Dry		15.30	3.825	76.5	0.49	0.122	2.4	78.9
Medium sand...	Moist	5.0	15.45	3.886	77.5	1.103	0.276	5.5	83.0
	Dry		14.75	3.687	73.7	0.48	0.120	2.4	76.1
Fine sand.....	Moist	7.5	28.51	7.127	95.0	1.56	0.390	5.2	100.2
	Dry		27.27	6.817	91.0	0.48	0.120	1.6	92.6
Very fine sand..	Moist	8.5	30.78	7.695	90.6	2.06	0.515	6.0	96.6
	Dry		29.26	7.315	86.0	0.703	0.176	2.3	88.3

* Average of four determinations.

A glance at tables 8 and 9 shows that the recovery of nitrate was less complete with the more dilute solution, the average percentage of recovery being 76.3 for the moist quartz and 70.7 for the oven-dry quartz, compared

TABLE 10

Nitrate removed from four grades of ground quartz

SIZE OF MATERIAL	CONDITION	NITRATE			SOLUTION REMAINING IN QUARTZ	NITRATE		SOLUTION REMAINING IN QUARTZ	NITRATE REMOVED		EXTRACTION OF SAND-NITRATE		NITRATE ACCOUNTED FOR
		Amount added	First extraction			Second extraction			First extraction	Second extraction			
			Found	Actually removed		Found	Actually removed						
		mgm.	*p. p. m.*	*mgm.*	*cc.*	*p. p. m.*	*mgm.*	*cc.*	*per cent*	*per cent*	*mgm.*	*per cent*	*per cent*
Coarse sand....	Moist	5.0	17.74	4.183	14.18	1.21	0.286	14.37	83.6	5.7	0.625	12.5	101.8
	Dry	5.0	15.30	3.583	15.84	0.49	0.115	15.84*	71.6	2.3	Trace		78.9
Medium sand..	Moist	5.0	15.545	3.675	13.53	1.103	0.259	14.8	73.5	5.2	1.023	20.46	99.2
	Dry	5.0	14.75	3.478	14.23	0.48	0.113	14.23*	69.5	2.3	Trace		76.1
Fine sand.....	Moist	7.5	28.51	6.680	15.72	1.56	0.368	14.06	89.0	7.5	0.917	10.79	107.2
	Dry	7.5	27.27	6.403	15.23	0.48	0.113	16.23*	85.3	2.3	Trace		92.6
Very fine sand..	Moist	8.5	30.78	7.187	16.54	2.06	0.480	17.15	84.6	9.6	0.826	9.7	103.9
	Dry	8.5	29.26	6.809	17.25	0.703	0.164	17.25*	80.1	3.5	Trace		88.3

* Weight not taken. Assumed to be same as after first extraction.

with 87.9 and 81.8 which are the corresponding figures for the more concentrated solution. Thus it is seen that the recovery from the oven-dry quartz was less in both cases, less by 5.6 per cent for the dilute solution and by 6.1 per cent for the more concentrated solution. This relationship holds throughout the second extraction also. This seems to indicate a real loss of nitrate due to heating in the oven for 8 hours at 105°C.

In order to test this point further, eight 10-cc. samples of a nitrate solution containing 100 parts per million and eight 5-cc. portions containing 500 parts per million were treated with a few drops of saturated sodium carbonate solution and evaporated to dryness on the water-bath. The nitrates in four samples of each were determined at once in the usual manner. The remaining four samples of each concentration were dried in the oven at about 105°C. for 8 and 21 hours, respectively. The results of all the determinations are given in table 11.

TABLE 11

Effect of heating at 105°C. on quantity of nitrate recovered from quartz sand

GRADE OF MATERIAL	CONCENTRATION			
	About 0 1 mgm. per cubic centimeter		About 0.5 mgm. per cubic centimeter	
	Not heated	After heating	Not heated	After heating
Coarse sand	40.125	43.75*	36.00	41.00
Medium sand	40.375	45.20*	37.25	41.00
Fine sand	40.750	45.40*	37.00	40.25
Very fine sand	40.000		37.25	40.50
Average	40.31	44.59	36.87	40.69
Percentage recovery	100.00	90.39	100.00	90.86

* Average of five readings, others average of four readings.

Since all of the above were compared with the same standard and all samples of each concentration were diluted to the same extent, the average colorimeter readings bear to each other exactly the same relationship as would the actual milligrams of nitrate, so the reading of unheated samples is considered 100 and the other found thus: $44.59 : 40.31 = 100 : x$. Of the weaker solution, 10 cc. was diluted to 1000 cc. and of the stronger, 5 cc., to 2500 cc. in order to bring each to approximately 1 part per million for reading. From these figures the total milligrams of nitrate in each can be calculated. These figures show a loss of nearly 10 per cent of the nitrate after the period of heating at slightly above the boiling point. This is in accord with the earlier work recorded in this paper. For this reason further discussion here will deal with the unheated materials only.

In the case of the coarse and medium grades with the same quantity of nitrate added, the medium holds more, or gives up less, nitrate at both

concentrations; the same relationship holds at both concentrations when we compare the nitrate recovered from the fine and very fine grades receiving, respectively, 15 and 17 cc. of nitrate solution. This tends to show that the difference is due to a surface effect.

Let us consider the very fine sand grade in tables 9 and 10. There was incorporated in this grade 8.5 mgm. of nitrate. The first extraction removed 7.187 mgm. of nitrate in the 233.46 cc. of drainage (table 10). Had the entire 250 cc. of diluted nitrate solution been a homogeneous mixture, this quantity of solution could have contained only 7.695 mgm. of the original 8.5 mgm. incorporated.

In the second extraction of this grade, 0.48 mgm. of the 1.313 mgm. actually remaining in the quartz, was removed in the 232.85 cc. of drainage. Had this second solution been homogeneous, 0.515 mgm. of nitrate would have been recovered, which still leaves 0.798[9] mgm. of nitrate to be accounted for.

How shall we account for the apparent failure of 0.805 mgm. of nitrate to go into solution in the first, and 0.798 mgm. in second extraction? To the writer there seems but one answer to this question, that of King (46). When the nitrate solution came in contact with the quartz particles, a definite attraction due to the force of adhesion was set up. The quantity of the more concentrated solution added was greater than the sand could hold by adsorption, so that when the distilled water was supplied the nitrate solution held mechanically only, formed a homogeneous mixture with the water when stirred. The 16.54 cc. of solution remaining in the quartz after the first extraction, if of the same composition as the 233.46 cc. removed, would have contained 0.508 mgm. of nitrate. This is 0.028 mgm. in excess of the 0.48 mgm. actually removed in the second extraction, or, 0.007 mgm. less than would have been contained in the 250 cc. of solution had it been of the same composition as that draining from the sand.

Since the dilution is so much greater in the second extraction, it may be expected that the outer part of the film, less strongly adhering to the particles would tend to form a homogeneous mixture with the water, this together with the nitrate solution held mechanically only, and that coming by diffusion from the strongly held film, furnishes the whole of the nitrate removed in the second extraction. King's data, table A (p. 177), shows that after six extractions the nitrate recovered is that coming from the strongly adhering film by diffusion.

Five months after the two extractions were made, the air-dry quartz samples which had stood in the laboratory in beakers covered with paper were themselves treated with phenoldisulfonic acid and nitrates determined in the usual way. The nitrate so determined is shown as milligrams and per cent of the total in the latter part of table 10. In no case did the samples which had been heated in the previous extractions show the presence of nitrates, while all

[9] 8.5 mgm. total; actually removed by first extraction, 7.187 mgm., or 1.313 mgm. remained; 1.313 − 0.515 = 0.798 mgm.

unheated samples contained considerable quantities of nitrates. No claim is made that the conditions under which these had been stored are such that the nitrate now recovered, together with that previously removed, should equal 100 per cent of the original quantity of nitrate used. However, it is notable that in all except the fine sand size the total recovery is nearly 100 per cent.

These data are not in accord with those of Noyes (71) who reports all nitrate recovered in one extraction nor with those of Bouyoucos (6), published since the above was written, who states that the soil solution is less concentrated at the immediate surface of the particles.

Under the conditions of this experiment, not all of the nitrate added to pure quartz nor to a soil containing but a faint trace of nitrate (white silt loam, table 6), was recovered in one extraction nor even in two extractions. While the data here reported are entirely too meager to warrant definite conclusions, yet it is significant that extracting the quartz itself brings the nitrate recovered so near 100 per cent of the total added.

This work corroborates in every important detail that of King (46) and though these data are meager they indicate clearly that with soils containing a moderately low percentage of capillary moisture, at, or slightly below optimum, much of the soluble salts are held in this film moisture. This film adheres so strongly to the particle that much of the soluble material it contains is given up to water on extraction by diffusion only and this explains, in part, the effect of air-drying. When the capillary moisture is lost the salts are left as minute crystals on the soil particles, and it is clear that quickly washing with water will bring these salts into solution so as to give a more homogeneous solution than can be obtained by washing a moderately moist soil in the same way.

When a soil is oven-dried we get all of the effect of air-drying just discussed, together with several additional effects. Heating at 105°C. coagulates the colloids. This the oven-dry samples showed very clearly, on working them with a pestle in the mortar. With the heavier soils much difficulty was encountered in making a "thin paste," as the soil adhered so tightly to both the pestle and the mortar. After heating, there was no tenacity whatever, a heavy silt or clay loam working as easily as did fine sandy loam. This action on the colloidal matter would enable the water to come into more intimate contact with the material which exposes the major part of the total surface of the soil. As already shown, Hulett and Allen (37), the particles of colloidal size are more soluble than larger ones. This effect on colloids is undoubtedly an important factor, and helps explain higher solubility in the soils with smallest particles.

Authors cited above hold that heating alters organic as well as inorganic materials in the soil, rendering them more soluble. While the physical factor in sands and silt loam has been shown to explain in part the increased recovery of salts due to heating, it seems to the writer that the effect on colloids and the well-known effect of heat in increasing the solubility of some minerals and organic matter also are important factors.

SUMMARY

1. Oven-drying increased to a marked degree the quantity of water-soluble material removed from soil by 1:5 extraction with distilled water.

2. Air-drying swamp soils increased the water-soluble material and oven-drying this air-dried soil brought about a still further increase.

3. Storing soils for 9 weeks at 8 to 12°C. in open jars (in which water evaporated was restored each week) or in sealed tubes in its original condition did not markedly affect the total soluble material. Nitrification occurred in the open jars, while nitrates decreased, as a rule, in the sealed tubes.

4. Keeping soil at room temperature and optimum moisture content for 9 weeks did not materially affect the amount of soluble material, but there was a slight increase in all soils except white silt loam. Keeping these soils saturated at the same temperature, greatly increased the soluble material. In the first case nitrification was active while in the latter, denitrification was complete.

5. Oven-drying decreased the nitrate-content of these soils.

6. When potassium nitrate in two concentrations was added to four grades of quartz, it was not wholly recovered in one, or even two 1:5 extractions. From the more dilute solution 67 to 80 per cent of the nitrate were recovered in one extraction, while from the more concentrated, 77 to 95 per cent were recovered.

7. When potassium nitrate in a dish is heated in an oven at 105°C. for 8 hours, after being evaporated to dryness, a distinct loss of nitrate occurs.

GENERAL CONCLUSIONS

The literature cited and the experimental work here reported both bring out one important point. They show the effect of drying at room temperature, and heating in an oven at slightly above the boiling point, and in the autoclave at various pressures and temperatures. In general, the quantity of soluble inorganic constituents and organic matter is increased, while temperatures above 100°C. reduce the quantity of nitrates. These facts indicate that in planning soil biology studies, pot-culture or other greenhouse fertility investigations, the soils used should be kept under conditions strictly comparable as to aeration, moisture content and temperature in order to avoid the introduction of uncontrolled factors which might lead to erroneous conclusions.

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SULFUR OXIDATION IN "BLACK ALKALI" SOILS[1]

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In 1916, Lipman (6)[2] made the suggestion that the change of sulfur to sulfuric acid in the soil caused by the action of microörganisms might be employed for converting sodium carbonate into sodium sulfate and making productive the barren alkali areas. Lipman and Sharp (5) showed in their studies of chemical treatment of alkali land that where about 50 tons of strong sulfuric acid were sprayed on 40 acres of alkali soil there was a decided improvement in the productive power of the soil, but not great enough to justify the sulfuric acid treatment in practice. Treatment with sulfur gave no results.

For the study of the behavior of inoculated sulfur in black alkali soils, two 200-pound samples of such soil were secured by courtesy of Professor Hoagland of the University of California. For information concerning one of the alkali soils the following data were given by Dr. Hoagland:

> This soil was obtained from the University Ranch near Fresno in the San Joaquin Valley, California. It came from a bad spot in a tract of 160 acres called the "experimental drainage tract." This land was originally productive but later ceased to produce crops on account of the accumulation of the so-called alkali salts. Some years ago an attempt was made to reclaim this soil by installing a tile drainage system five or six feet deep and by flooding twice with an excess of good irrigation water. An attempt was then made to grow a barley crop but it was found that the reclamation was not successful as less than one-half of the land was capable of even fair production. Many spots were bare. . . . . Our present information leads us to believe that it is almost impossible to remove the toxic alkalinity from this soil by ordinary washing. It undoubtedly contains various alkaline substances including sodium carbonate, sodium silicate, sodium organic compounds, etc. The physical state of the soil is exceedingly bad.

The given information is undoubtedly about soil no. 17 for, although this soil will not support any ordinary growth as has been repeatedly tried with different crops in the greenhouse, and although it has a high alkalinity and a high content of alkali salts, the alkalinity and the amounts of salts are not as high as in soil no. 16. Moreover, soil no. 17 has a decidedly lower chlorine content than soil no. 16. Both the soils are sandy loam soils with a very

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[2] In the course of a study on sulfur oxidation Dr. J. G. Lipman suggested the work reported in this paper

fine structure. This can be seen from the data given in table 1, showing the results of the mechanical analyses of these soils.

The poor structure of this soil as well as the high alkalinity prevents ordinary crops from taking hold, so in addition to changing the alkalinity, the structure ought to be improved simultaneously.

Chemical analyses of these soils were made only so far as seemed necessary for the scope of the study. K_2O, P_2O_5, Cl, N, SO_4, Ca and total alkalinity were determined. Alkalinity was determined by titration and hydrogen-ion concentration methods.

TABLE 1

Mechanical analyses of soils number 16 and 17

NAME OF FRACTION	NO. 16	NO. 17
	per cent	*per cent*
Fine gravel	4.94	5.21
Coarse sand	11.14	12.07
Fine sand	7.85	9.56
Very fine sand	28.10	31.52
Silt and clay	47.56	41.42

INFLUENCE OF SULFUR OXIDATION ON THE ALKALINITY OF THE SOILS

To these soils was added inoculated sulfur in amounts varying from 100 to 3500 pounds per acre, and the highest amounts of sulfur added were calculated to be adequate for the neutralization of the high alkalinity of soil no. 16. The different applications were made for the purpose of determining whether or not sulfur oxidation would occur in smaller quantities in these soils evidently toxic to the biological flora and to plant growth. Although the same quantities of sulfur were applied to soil no. 17, the greater amounts were more than necessary to neutralize the alkalinity of the soil.

The soil samples were thoroughly mixed with the inoculated sulfur, and were then placed in tumblers covered with glass plates. The tumblers with contents were weighed and the water-holding capacity of the soil determined. The soils were kept at 60 per cent of their water-holding capacity throughout the experiment and incubated at 28°C.

During the incubation period a record was kept of the changes in hydrogen-ion concentrations, which for soil no. 16 are recorded in table 2.

It can be seen at once that the smallest sulfur applications exerted little or no influence on the change of the hydrogen-ion concentration, but the higher amounts of inoculated sulfur brought about a decided lowering of the hydrogen-ion concentration. However, after an incubation period of 30 weeks, the neutral point was not yet reached.

Much more pronounced were the changes of the hydrogen-ion concentration caused by sulfur oxidation in soil no. 17, which changes are reported in table 3.

The changes in hydrogen-ion concentration occurring during the relatively short incubation period of 12 weeks were such that in several cultures the neutral point was reached before, or at the end of this period. This indicated that if sufficient sulfur is added, the sulfur changing to sulfuric acid could be

TABLE 2

Changes in hydrogen-ion concentrations of water extracts from soil no. 16 during the period of incubation

CULTURE NO	SULFUR APPLIED	INITIAL pH VALUE	pH VALUES AFTER VARYING PERIODS OF INCUBATION									
			2 weeks	3 weeks	5 weeks	6 weeks	8 weeks	9 weeks	11 weeks	12 weeks	18 weeks	30 weeks
	lbs. per acre											
12	None	9.8	9.7	9.7	9.8	9.9	9.9	9.9	9.7	9.6	9.6	9.6
13	100	9.8	9.7	9.6	9.5	9.8	9.8	9.8	9.6	9.7	9.6	9.6
14	300	9.8	9.4	9.5	9.5	9.7	9.8	9.8	9.6	9.6	9.6	9.6
15	500	9.8	9.4	9.6	9.6	9.8	9.8	9.7	9.7	9.6	9.5	9.5
16	1000	9.8	9.5	9.5	9.6	9.8	9.7	9.8	9.7	9.3	9.3	9.4
17	1500	9.8	9.8	9.7	9.6	9.6	9.6	9.6	9.5	9.3	9.3	9.3
18	2000	9.8	9.7	9.5	9.4	9.3	9.3	9.3	9.4	9.2	9.2	9.2
19	2250	9.8	9.7	9.4	9.2	9.3	9.3	9.3	9.4	9.1	8.8	8.7
20	2500	9.8	9.8	9.4	9.3	9.3	9.3	9.2	9.1	9.0	8.6	8.7
21	3000	9.8	9.6	9.4	9.3	9.2	9.2	9.3	9.1	8.9	8.2	8.2
22	3500	9.8	9.8	9.8	9.8	9.7	9.5	9.3	8.7	8.2	8.0	8.0

TABLE 3

Changes in hydrogen-ion concentrations of water extracts from soil no. 17 during the period of incubation

CULTURE NO.	SULFUR APPLIED	INITIAL pH VALUE	pH VALUES AFTER VARYING PERIODS OF INCUBATION									
			2 weeks	3 weeks	5 weeks	6 weeks	8 weeks	9 weeks	11 weeks	12 weeks	18 weeks	30 weeks
	lbs. per acre											
23	None	9.2	9.1	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
24	100	9.2	9.2	9.2	9.2	9.0	9.0	9.0	8.9	8.8	8.8	8.8
25	300	9.2	9.2	9.1	9.0	9.0	9.0	9.0	8.8	8.6	8.6	8.6
26	500	9.2	9.0	8.7	8.9	9.0	8.9	9.0	8.6	8.4	8.4	8.4
27	1000	9.2	9.0	8.6	8.3	8.6	8.5	8.5	8.2	8.0	8.0	8.1
28	1500	9.2	8.8	8.1	7.8	7.7	7.4	7.4	7.4	7.4	7.6	7.8
29	2000	9.1	7.7	7.8	8.0	8.1	8.1	8.0	7.9	7.4	7.4	7.6
30	2250	9.0	7.6	7.5	7.4	7.3	7.3	7.3	7.2	7.0	6.9	7.3
31	2500	8.9	7.5	7.4	7.6	7.5	7.4	7.3	7.3	7.0	6.9	7.2
32	3000	8.9	7.4	7.4	7.4	7.3	7.2	7.1	7.0	6.8	6.6	7.0
33	3500	9.0	7.5	7.4	7.3	7.2	7.0	6.9	6.3	6.6	6.4	6.7

employed to convert the sodium carbonate into sodium bicarbonate and sodium sulfate. The results from inoculated sulfur applications would be noticed within a reasonably short time, provided the soil had been subjected to leaching previous to the sulfur treatment. It is interesting to notice

that in both soils very little change in reaction took place after 12 weeks, not even in the cultures treated with the larger quantities of sulfur. In fact the process of oxidation seemed nearly completed after this period. It seems, therefore, that in neutralizing the soil a somewhat greater quantity of sulfur is necessary than the amount theoretically calculated.

These experiments were repeated with a second lot of two samples of about 100 pounds each, sent by courtesy of Dr. Hoagland from the same place. The soils were again labelled 16 and 17. For convenience they will be referred to as numbers 16a and 17a. These experiments were conducted in the greenhouse with glazed earthenware pots having a capacity of 2.5 kgm. The experiments were conducted during the months of November to April.

To the soils were added the following quantities of sulfur:

CULTURE NO.	POUNDS PER ACRE	CULTURE NO.	POUNDS PER ACRE
1 and 10	None	6,15	2000
2 and 11	300	7,16	2500
3 and 12	500	8,17	3000
4 and 13	1000	9,18	3500
5 and 14	1500		

The pots were left standing on a bench in the greenhouse and watered at intervals, but no care was taken to keep the soils at an optimum moisture content. Soon heavy salt incrustations were formed at the surface, but the soil was not stirred and no attempt was made to remove the crystalized salts other than by adding water. This may explain why slight irregularities occured in the readings of the hydrogen-ion concentrations. For sampling, a wide cork borer was used and care was taken to have a column of soil from top to bottom, without destroying the layer of salts on top of the soils.

The changes in hydrogen-ion concentration recorded are reported in table 4.

The changes of hydrogen-ion concentration in these soils placed in pots were very similar to the changes brought about by inoculated sulfur in the tumblers kept at a supposed optimum moisture content and a regulated temperature. Slight changes took place in the soils to which 300 and 500 pounds of sulfur to the acre were added until the end of the eight or the end of the tenth week, particularly in soil no. 17a. After this time the hydrogen-ion concentration became less, and returned toward the original concentration. As could be expected the higher application of sulfur exerted a far greater influence on the change of the hydrogen-ion concentration than the small amounts added. After 12 weeks the neutral point was reached in the case of soil no. 17a to which 3500 pounds of sulfur was added, and where smaller quantities of sulfur were applied the hydrogen-ion concentration approached the neutral point.

These soils do not support any ordinary plant growth. An attempt was made to determine at what hydrogen-ion concentration barley seedlings would survive and start to grow. Every 14 days barley seedlings were planted in all pots, during the first 10 weeks without being able to keep the seedlings alive. In the soils to which large quantities of sulfur were added the plantlets made considerable growth but because of the small capacity of the pots and the imperviousness of the soil the plants were injured by the salt solution concentrating at the surface of the soil. The pots were watered frequently and the water added dissolved the hard alkali incrustations formed on

TABLE 4

Changes in hydrogen-ion concentrations of soils no. 16a and 17a treated with inoculated sulfur and placed in the greenhouse

SOIL NO.	CULTURE NO.	SULFUR APPLIED	INITIAL REACTION	pH VALUES AFTER VARYING PERIODS OF INCUBATION										
				1 week	3 weeks	5 weeks	6 weeks	7 weeks	8 weeks	10 weeks	11 weeks	12 weeks	18 weeks	24 weeks
		lbs. per acre												
16a	1	None	9.6	9.6	9.6	9.6		9.6		9.6	9.6	9.6	9.6	9.6
	2	300	9.6	9.4	9.4	9.4		9.6		9.0	9.1	9.2	9.0	9.1
	3	500	9.6	9.4	8.9	9.0		8.9		8.8	8.9	9.1	8.9	8.9
	4	1000	9.6	9.4	9.4	8.9		9.0		8.4	8.5	8.6	8.3	8.4
	5	1500	9.6	9.4	8.9	8.7		8.4		8.2	7.9	7.6	8.0	7.7
	6	2000	9.5	9.4	8.8	8.1		8.0		8.0	7.9	7.9	8.1	7.7
	7	2500	9.6	9.4	8.6	8.1		8.1		7.7	7.6	7.6	8.0	7.6
	8	3000	9.6	9.5	8.5	7.9		8.1		7.5	7.6	7.7	8.0	7.5
	9	3500	9.6	9.5	8.2	7.7		8.0		7.6	7.6	7.5	7.3	7.1
17a	10	None	9.2	9.2	9.0	9.2	9.1	9.2	9.0		9.0	9.2	9.2	9.3
	11	300	9.2	9.2	9.2	9.1	9.0	8.8	8.6		9.0	9.2	9.0	9.1
	12	500	9.1	9.2	9.0	8.9	9.0	8.6	8.6		9.0	9.1	9.1	9.1
	13	1000	9.2	9.1	8.9	8.6	8.8	8.4	8.4		8.8	8.6	8.7	8.6
	14	1500	9.2	9.1	9.1	8.7	8.6	8.0	8.0		7.7	7.9	8.4	8.4
	15	2000	9.2	9.1	9.0	8.5	8.6	8.0	8.0		8.0	7.9	8.3	7.6
	16	2500	9.1	9.2	9.0	8.4	8.4	7.7	7.5		7.4	7.5	7.6	7.5
	17	3000	9.1	9.2	8.8	8.2	8.2	7.9	7.5		7.3	7.4	7.7	7.5
	18	3500	9.1	9.1	8.7	8.2	8.1	7.5	7.3		6.6	6.8	7.0	6.8

top of the soil. Because of the poor physical condition of the soil this solution remained on the surface a considerable length of time and finally killed the plantlets.

Barley seeds were then planted, and they germinated well in soil no. 17a receiving 1500 pounds or more of sulfur per acre. Only a few seeds germinated in soil no. 16a to which 2500 or more pounds of sulfur per acre was applied. All these seedlings grew well, had a very dark green color, but most of them were not able to survive the injury caused by the repeated flooding and consequent attack of the concentrated salt solution. It seems reasonable to

expect far better results in the field, or in pots with a device to take care of the watering or at least of the surplus of water. These soils have an extremely poor structure and would be difficult to handle even without injurious "alkali" salts.

INFLUENCE OF SULFUR OXIDATION ON THE BIOLOGICAL FLORA

For the study of the biological changes, infusions were made from soils no. 16 and 17, incubated at 28°C., and plated out on Lipman and Brown's agar at the beginning of the experiment, after 6 weeks, after 12 weeks, and after 18 weeks. The biological flora for these soils expressed in numbers of colonies growing on agar plates as an average of three plates counted is given in table 5.

TABLE 5

Bacterial numbers in soil no. 16 and 17 treated with inoculated sulfur (in thousands per gram)

SULFUR APPLIED, (*lbs. per acre*)	NONE	100	300	500	1000	1500	2000	2250	2500	3000	3500
Culture No.....	1	2	3	4	5	6	7	8	9	10	11
Soil no. 16											
Before treatment.....	60	58	64	62	63	60	59	60	58	62	60
After 6 weeks.....	61.5	30	35	65	50	60	181	231	230.5	226	255
After 12 weeks.....	69	75	105.5	125.5	107	112.5	208	251	302	348	411
After 18 weeks.....	70	74	102	116	122	158	241	306	388	492	627
Soil no. 17											
Before treatment.....	335	332	333	334	335	332	318	329	326	334	329
After 6 weeks.....	330	325	320	275	260	250	225	255	250	235	255
After 12 weeks.....	435	442	490	540	630	960	1700	1225	1550	1600	2100
After 18 weeks.....	440	448	520	620	752	1110	1720	1542	1832	2540	2940

It seems evident that the numbers of colonies growing on agar plates varied directly as the hydrogen-ion concentration. The rate of increase was very much the same for both soils.

The increase in colonies was quite consistent with the increase of the amount of sulfur added. Still, the highest numbers obtained were relatively small if compared with the numbers present in ordinary soils. The numbers in the untreated incubated soils seemed to increase slightly, as could be expected from the favorable temperature and moisture content. After an incubation period of 12 weeks, the soil receiving 3500 pounds of sulfur per acre, was found to produce approximately five times as many colonies per plate as the untreated soil. The numbers for the cultures with the higher sulfur applications for soil no. 17 were from three to five times greater.

It was noted throughout all the experiments in the three different soils to which certain quantities of sulfur were added that a relatively large number

of tiny white colonies of actinomycetes appeared on the surface of the soil. In fact, if the soils were very acid or extremely alkaline, the counts made on the agar plates usually consisted for the most part of molds and actinomycetes. The molds predominated in the cultures to which very small amounts of sulfur were added and the actinomycetes in the cultures with greater quantities of sulfur. Often two-thirds or even four-fifths of the colonies on the plates inoculated with infusions from the soil with the lower sulfur applications, were molds and actinomycetes. In the alkaline soil no. 17 to which larger amounts of sulfur were added and which reached or approached the neutral point but a very small number of the total colonies counted consisted of molds and actinomycetes. It was surprising to notice the difference which occured. Nevertheless, not a great variety of biological flora was present.

INFLUENCE OF SULFUR OXIDATION ON THE PHYSICAL STRUCTURE OF THE SOILS

The influence of chemicals, salts and various substances upon soils has been studied in innumerable instances. There is no doubt about the important part played by the various constituents added to a soil. The work reported in this part of the paper was carried out mainly to study the change in the physical structure of the soils when inoculated sulfur was added, and transformed into sulfates. In the course of the biological and vegetation experiments it was frequently noticed that the soil, to which different amounts of sulfur were added, had a tendency to form small aggregates, resulting in making the soils apparently more porous.

Unfortunately no good methods are available for measuring accurately the changes in granulation. The methods employed to estimate small differences caused by additions of salt could not be used on account of obvious obstacles. An attempt was made to determine differences in granulation, produced as a result of sulfur oxidation, by screening the soils, but slight differences in the moisture contents of the soils produced greater errors than the differences found between the soils treated with varying amounts of inoculated sulfur. Drying the soils in the oven made no difference in the size of the errors.

An effort made to measure the differences in cohesion of the soils as described by Cameron and Gallagher (1), and again by Davis (2), by means of an apparatus for measuring penetration, failed likewise to gave reliable results.

Patten and Waggaman (7) have shown that adsorption of soluble material exerts an appreciable influence upon the water-holding power of finely divided soils. The hydroxides and carbonates seemed to lower the water-holding capacity and other salts to raise it. An attempt was made to determine the influence of the formation of sulfates in the soils, upon the water-holding capacity.

The endeavor to measure the formation of aggregates, by measuring the capillary rise of water, failed because the soils had to be packed closely thereby destroying the small aggregates formed.

The measured changes from carbonates into bicarbonates, flocculation and turbidity measurements can hardly bring out the phenomonon of aggregate formation. Determinations of apparent specific gravity of the treated and untreated soils also are apt to produce errors, even if the samples are previously dried, since slight differences in the initial percentage of water may cause irregularities.

Nevertheless, all these interdependent factors together can give some idea of the changes caused by the oxidation of elemental sulfur into sulfates by microörganisms.

Methods

Water-holding capacity determinations of the treated and untreated soil were made according to the Hilgard (3) method after 12 weeks of incubation. Averages of three determinations are given in the tables.

The method used to determine the change in apparent specific gravity of the soils was that of weighing, full of soil, a vessel whose volume was known. The dried soil was allowed to fall through a coarse wire creen until it overran the edges of the cup, and was then carefully leveled to the top of the cup with the edge of a spatula as recommended by Davis (2). After weighing the cup and soil, the top of the soil was taken off and a representative sample of the interior of the mass placed in a weighing bottle and the moisture determined by heating for 15 hours at 105 to 108°C. Triplicate moisture determinations showed that but little difference occurred between the previously dried samples, and an average of these three determinations was taken as a basis for calculations.

Determinations of apparent specific gravity on samples not previously dried showed greater differences but were discarded. At least two determinations were made of all samples.

Flocculation of the soil was determined by shaking 2 gm. of soil with 50 cc. of distilled water using burettes as containers, and measuring as accurately as possible the amount of the clear or transparent liquid, after standing for 24 hours.

For the turbidity measurements, one part of soil was mixed with two parts of water, the soil suspensions were poured into burettes, and after 24 hours the upper 10 cc. was carefully pipetted off into weighing dishes and the total residue estimated after evaporation and drying at 100°C. as has been suggested by Hoagland and Martin (4).

Total alkalinity and bicarbonates were determined by making water extractions of 20 gm. of air-dried samples of each soil. The samples were shaken with 200 cc. of distilled water in a shaking machine for 2 hours. The flasks were left standing over night and filtered until the liquid was clear or transparant without sediment. An aliquot was titrated with 0.02*N* sulfuric acid with methyl red and phenolphtalein as indicators.

In the cases of the alkali soils a few cubic centimeters of concentrated hydrochloric acid were added to the remainder of the liquid to aid settlement of possible small quantities of colloidal matter.

Soluble sulfate formed was determined in aliquots of the liquid to which was added 2 cc. of concentrated hydrochloric acid, by precipitating at the boiling point with barium chloride.

Experimental results

A. Soil No. 1

In order to be able to compare the results obtained from the alkali soils with a productive soil there was included a series of cultures of a good Hanford sandy loam. This soil was taken from an orange grove, which had been manured annually with barnyard manure. It was slightly alkaline by the hydrogen-ion method, having a pH value of 7.2. It was neutral with the Veitch method, but after shaking for several hours in the shaking machine the liquid had a total titratable alkalinity of 0.21 cc. of 0.1 *N* H_2SO_4 per 10 gm. of soil.

The formation of sulfate in soils treated with inoculated sulfur is influenced by the water content of the soil. Experiments were carried out to determine at which point of water saturation sulfur oxidation would reach the optimum for the soils used when at a temperature of 28°C. It was found that oxidation increased with the increase of moisture until approximately 55 per cent of the amount necessary for complete saturation was reached. From then on oxidation decreased slowly to about 70 per cent of the water-holding capacity. When larger quantities of water were added hydrogen sulfide began to develop, which could easily be detected by the smell and sometimes even by the black color produced in the mixtures.

It was found in earlier experiments that sulfur oxidation proceeded more rapidly at a temperature of 30°C. than at room temperature. The cultures under discussion were kept at 28°C. throughout the experiments. This temperature, however, does not necessarily mean best for most rapid sulfur oxidation.

The data given in table 6 show that with the increase of the amount of inoculated sulfur an increase occured in water-soluble sulfates. The increase obtained, however, was not proportional to the increase of sulfur added, as is reported in another table.

With the increase of sulfate accumulation the titratable acidity naturally increased.

The soil to which inoculated sulfur was added seems to assume a new set of physical properties, characterized by a more or less complete flocculation. The increase of sulfate accumulation was nearly proportional to the increase in flocculation, which is very rapid when greater quantities of sulfur are employed. From the data presented it is evident that there exists a good cor-

relation between the quantities of suspended material as measured by the transparent liquid column, the quantities of this material weighed after drying (turbidity), and the amounts of sulfur oxidized.

A number of investigators have set forth the influence of various hydroxides, carbonates, phosphates, sulfates, etc. upon the water-holding power of soils. Although the results obtained are irregular, there seems to be a general tendency to decrease the water-holding capacity with the increase of sulfates formed.

The data obtained and presented in table 6 for the changes in apparent specific gravity seem to indicate that the formation of sulfates caused the soil to increase in volume up to a certain point. After this point was reached the volume decreased again. It should be born in mind, however, that not

TABLE 6

Formation of sulfates, changes in total acidity, flocculation, turbidity, water-holding capacity and apparent specific gravity in soil no. 1, after 12 weeks of incubation

CULTURE NO.	SULFUR APPLIED	SULFATE*	TOTAL ACIDITY IN TERMS 0.1 *N* NaOH*	FLOCCULATION MEASURED BY TRANSPARENT LIQUID	TURBIDITY MEASURED BY RESIDUE IN SOIL SUSPENSION	WATER-HOLDING CAPACITY	SPECIFIC GRAVITY
	lbs. per acre	*mgm.*	*cc.*	*cc.*	*mgm.*	*per cent*	
1	None	1.07	0.02	7.5	24.2	31.9	126.83
2	100	2.39	0.05	8.0	23.9	32.7	126.02
3	300	5.38	0.20	8.0	22.9	31.3	126.22
4	500	7.15	0.28	11.5	18.4	31.2	124.32
5	1000	15.68	0.30	12.0	13.2	31.4	123.12
6	1500	17.92	0.32	12.2	6.2	33.1	118.17
7	2000	20.52	0.40	14.1	4.7	31.4	113.08
8	2250	19.08	0.40	16.3	2.0	27.5	113.08
9	2500	24.20	0.50	24.2	2.2	28.7	114.81
10	3000	24.86	0.60	32.4	1.9	29.0	116.08
11	3500	27.80	0.64	50.0	1.8	28.6	118.27

* Per 10 gm. of soil.

all the sulfur added had been oxidized, and the quantities of oxidized sulfur necessary to bring about greatest increase in volume may be different from the quantities applied where this point was observed and as is indicated by the figures in the table.

B. Soil No. 16

The oxidation of sulfur as indicated by the water-soluble sulfates increased with the increase of the quantities of inoculated sulfur employed as shown in table 7.

It is very evident that the carbonates were transformed into bicarbonates with the decrease in alkalinity. It is obvious that the toxic carbonates were changed to a great extent. In fact, almost all titrated alkalinity in the soil to which the largest amount of sulfur was added, had been converted into

bicarbonates, although the neutral point, with phenolphtalein as indicator, was by no means reached at the end of an incubation period of 12 weeks, and high alkalinity and large amounts of salts still prevailed. The soil extract was nearly neutral to methyl red.

With the decrease of alkalinity an increase in flocculation occurred, but this increase was, if compared with soil no. 1, not very large. The figures showing turbidity measurements include the salts present after shaking with distilled water for 2 hours in a shaking machine, and therefore, do not represent the true turbidity, since the drying of the residue does not remove the salts present. It was thought better not to try to deduct the amounts of

TABLE 7

Formation of sulfates and bicarbonates, changes in total alkalinity, flocculation, turbidity, water-holding capacity and apparent specific gravity in soil no. 16, after 12 weeks of incubation*

CULTURE NO.	SULFUR APPLIED	SULFATE†	BICARBONATES IN TERMS OF 0.02 *N* H_2SO_4	TOTAL ALKALINITY IN TERMS OF 0.1 *N* H_2SO_4†	FLOCCULATION MEASURED BY TRANSPARENT LIQUID	TURBIDITY (SALTS INCLUDED) MEASURED BY RESIDUE IN SOIL SUSPENSION	WATER-HOLDING CAPACITY	SPECIFIC GRAVITY
	lbs. per acre	*mgm.*	*cc.*	*cc.*	*cc.*	*mgm.*	*per cent*	
12	None	9.71	1.04	4.68	1.0	231.2	28.2	123.72
13	100	13.98	1.00	4.60	1.5	231.4	28.2	123.02
14	300	14.26	1.98	4.61	1.7	231.0	27.3	122.30
15	500	14.88	1.82	4.58	4.0	230.4	27.7	121.98
16	1000	15.72	1.72	4.52	4.0	230.0	26.6	121.55
17	1500	16.76	2.04	4.52	6.1	229.6	28.2	120.44
18	2000	26.32	2.54	4.47	5.2	229.0	28.9	118.88
19	2250	35.79	2.86	4.47	6.2	227.0	30.0	120.38
20	2500	37.38	2.79	4.32	7.1	227.1	28.0	115.96
21	3000	39.02	2.78	4.20	7.3	221.5	27.9	117.11
22	3500	42.38	3.20	3.60	9.2	221.0	30.7	115.38

* After the work was completed a short paper appeared in Soil Science, v. 9, p. 385, by P. L. Hibbard, showing the effect of sulfur oxidation on the reduction of alkalinity in alkali soils. Hibbard's titration data agree in general with the figures given in this table.

† Per 10 gm. of soil.

salts present by calculation, since the quantities of salts in the liquid after shaking would be necessarily different for the different cultures on account of the sulfur oxidized. Still, an appreciable decrease in turbidity occured, the weighed amounts gradually decreasing with the increase of the quantities of sulfur added.

The apparent specific gravity decreased with the increase of sulfate formation, being 9.3 per cent less for culture no. 22 as compared with culture no. 12.

C. Soil No. 17

Although sulfur oxidation did not seem to be greater in soil no. 17 than in soil no. 16, a number of cultures were neutral toward phenolphtalein at the

end of the incubation period. The former soil, having been leached, is considerably less alkaline and this accounts for the fact that much less inoculated sulfur was necessary to produce neutrality or even acidity after such a comparatively short incubation period. The remaining alkalinity in cultures no. 29 to 31 after 12 weeks was due to bicarbonates, and with the advance of sulfur oxidation the cultures gradually become neutral to phenolphtalein.

The turbidity measurements indicate that the physical structure of the soil was changed materially through the addition of inoculated sulfur.

The water-holding power of this soil seemed also to be changed, and the apparent specific gravity was decreased to a considerable extent, showing that there had been a formation of aggregates as a result of the sulfur oxidation. The changes under discussion are recorded in table 8.

TABLE 8

Formation of sulfates and bicarbonates, changes in total alkalinity, flocculation, turbidity, water-holding capacity and apparent specific gravity in soil no. 17, after 12 weeks of incubation*

CULTURE NO.	SULFUR APPLIED	SULFATE†	BICARBONATES IN TERMS OF 0.02 *N* H_2SO_4	TOTAL ALKALINITY IN TERMS OF 0.1 *N* H_2SO_4†	FLOCCULATION MEASURED BY TRANSPARENT LIQUID	TURBIDITY (SALTS INCLUDED) MEASURED BY RESIDUE IN SOIL SUSPENSION	WATER-HOLDING CAPACITY	SPECIFIC GRAVITY
	lbs. per acre	*mgm.*	*cc.*	*cc.*	*cc.*	*mgm.*	*per cent*	
23	None	7.65	1.00	3.52	0.5	98.0	27.2	124.62
24	100	9.11	1.76	3.02	1.5	94.1	27.4	123.92
25	300	13.42	0.72	2.40	3.0	87.2	27.1	121.40
26	500	16.10	0.92	1.80	1.5	79.0	29.2	121.20
27	1000	17.19	1.02	1.50	2.5	71.3	27.8	118.70
28	1500	20.27	1.02	1.20	5.0	65.1	28.5	118.33
29	2000	23.37	0.40	0.40	8.0	59.2	32.0	116.15
30	2250	34.59	0.40	0.40	16.2	54.0	33.3	116.34
31	2500	39.10	0.20	0.21	31.1	52.0	33.2	113.27
32	3000	42.06	0.00	0.00	47.2	43.2	34.9	114.61
33	3500	43.48	Acid	Acid	48.1	37.1	32.0	113.84

* See note at bottom of table 7.

† Per 10 gm. of soil.

The formation of sulfates may be directly responsible for the forming of aggregates but it is likely that the changes in the physical structure of all three soils under discussion is caused by the interrelated factors as the changes in microbiological flora, sulfate formation, conversion of carbonates into bicarbonates, and a possible interchange of bases in the soil.

The interdependence of the different phenomona recorded in the tables is brought out very strikingly in the graphs of figure 1. The curves representing sulfate formation are inverted to show the relation more clearly.

The exact quantities and percentages of inoculated sulfur oxidized, as far as they are changed into the water-soluble form, at the end of an incubation period of 12 weeks for the different cultures under discussion, are given in table 9.

In several instances sulfur oxidation in soils no. 16 and 17 had apparently been greater than in soil no. 1, especially in the cultures to which larger amounts of inoculated sulfur had been applied. It may be that in some instances not all soluble sulfates were removed by the shaking or that small

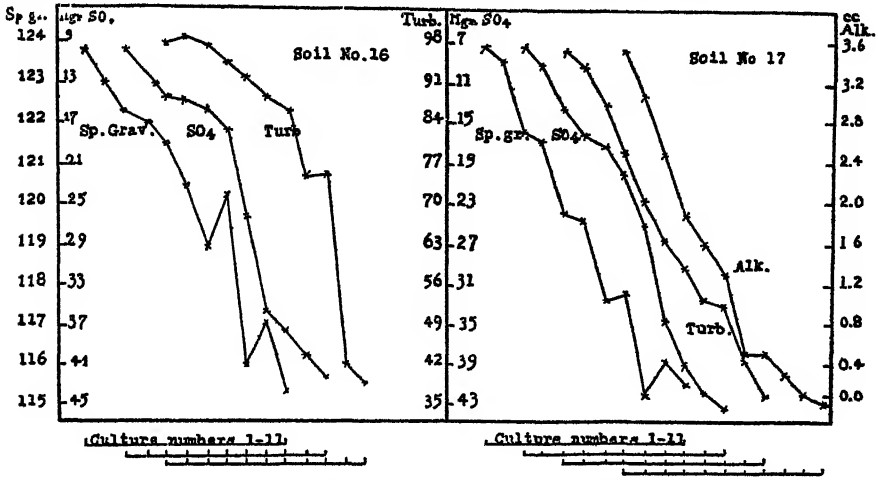

FIG. 1. CURVES REPRESENTING APPARENT SPECIFIC GRAVITY, SULFATES FORMED, TURBIDITY, AND CHANGES IN ALKALINITY OF SOILS NUMBERS 16 AND 17 AFTER AN INCUBATION PERIOD OF 12 WEEKS.

Abscissae represent culture numbers 1 to 11. To facilitate reading, the curves are placed next to each other instead of superimposing them.

TABLE 9

Quantities of inoculated sulfur oxidized in 100 gm. soil at the end of the incubation period of 12 weeks

CULTURE NO.	SULFUR APPLIED	SOIL NO. 1, SULFUR OXIDIZED		SOIL NO. 16, SULFUR OXIDIZED		SOIL NO. 17, SULFUR OXIDIZED	
	mgm.	*mgm.*	*per cent*	*mgm.*	*per cent*	*mgm.*	*per cent*
1	5	4.4	88.0	4.7	94.0	3.0	60.0
2	15	14.7	98.0	15.0	100.0	14.5	96.7
3	25	24.1	96.4	17.2	68.9	20.3	81.2
4	50	50.3	100.6	20.0	40.0	37.2	74.4
5	75	56.2	74.9	23.5	31.3	42.8	57.1
6	100	64.8	64.8	58.7	58.7	52.4	52.4
7	112	60.0	53.6	86.9	77.5	89.8	80.1
8	125	77.1	61.7	95.6	76.4	103.8	83.0
9	150	79.3	52.8	97.7	65.1	113.7	75.8
10	175	89.1	50.9	108.9	62.2	119.4	68.3

amounts of calcium sulfate, which are practically insoluble in distilled water, were formed. It can be seen from this table that but 50 to 60 per cent of the larger quantities of sulfur added had been oxidized in soil no. 1, whereas about 70 to 80 per cent of sulfur was oxidized in soil no. 17 to which the same quantities of sulfur were added.

Nearly all of the small amounts of sulfur added had been oxidized in all cultures. After 18 weeks the added sulfur had been oxidized in all cultures to an extent of 88 to 96 per cent, so that oxidation was practically completed at that time. It is obvious that in soil no. 17 a close relation exists between the readings of the pH values and the amounts of sulfur oxidized. The neutral point was reached after 81.5 per cent of the sulfur added to culture no. 8 was oxidized. This was approximately the amount of sulfur calculated necessary to neutralize the alkalinity of the soil. The cultures to which a surplus of sulfur was added and in which more than the amounts theoretically necessary were oxidized, showed acidity, although this acidity by the titration method hardly could be detected.

In soil no. 16 alkalinity still remained in all cultures, but the percentage of sulfur oxidized had also a great influence on the changes of the hydrogen-ion concentration. It seems that in all cases in these three soils the rate of oxidation was not entirely dependent upon the amounts of sulfur added, although the larger quantities naturally changed the high alkalinity more and at a faster rate.

SUMMARY

The soil to which inoculated sulfur is added seems to assume, through the formation of sulfates, a new set of physical properties characterized by a more complete flocculation, and changes in water-holding power and apparent specific gravity.

In "black alkali" soils small amounts of sulfur exerted little or no influence upon the hydrogen-ion concentration, but larger quantities brought about a decided change. The changes were similar in cultures kept in an incubator at 28°C. and at an optimum moisture-content, and in cultures kept in glazed earthenware pots in the greenhouse which were watered at indefinite intervals.

The leached soil was more readily neutralized by the addition of inoculated sulfur than the unleached soil, as indicated by titration and hydrogen-ion concentration methods. After 18 weeks the added sulfur had practically been oxidized in all cultures.

Carbonates were transformed into bicarbonates with the increase in sulfur oxidation. Although high alkalinity was changed into less alkalinity, high salt contents remained since no leaching occurred.

There was a striking relation between the sulfate formation and the flocculation, turbidity and apparent specific gravity of the leached and unleached soils. Sulfate formation tends to cause aggregation of this black alkali and Hanford sandy loam used, and the water-holding power seems to be changed.

The biological flora expressed in numbers of colonies grown on agar plates varied directly with the change in hydrogen-ion concentration. The cultures with the unleached soil, which received sufficient amounts of inoculated sulfur to neutralize the alkalinity, produced after 12 weeks of incubation, 5 times as many colonies per plate as did the untreated cultures, and the treated cul-

tures of the leached soil from 3 to 5 times as many colonies as the untreated cultures. After 18 weeks these cultures in both soils produced approximately 10 times as many colonies as did the untreated cultures.

The biological flora changed with the increase of the hydrogen-ion concentration. In the leached soil cultures, which reached or approached the neutral point after sulfur application, there were but relatively few colonies of molds and actinomycetes, whereas the colonies counted on agar plates made from infusions of untreated soil, consisted largely or nearly entirely of molds and actinomycetes.

Barley seeds germinated and grew readily in alkali soil treated with inoculated sulfur, but the plantlets were always killed by the salt incrustations on top of the soil, which dissolved when the pots were watered, while the water penetrated the soil but slowly on account of its poor physical condition.

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FACTORS INFLUENCING THE DETERMINATION OF SULFATES IN SOIL

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Many methods have been proposed for the determination of sulfates. Some are ideal for the purpose for which they were originated, but if they are applied to other substances or used under other conditions they do not give accurate results. Some of the methods are cumbersome and complex and consume considerable time. The methods may be divided into two classes, namely, the gravimetric and the volumetric. The gravimetric method depends on the low solubility of barium sulfate. The dissolved sulfate is treated with an excess of a soluble barium salt, the chloride, the nitrate, or the hydroxide—although the chloride is usually used—and the precipitated barium sulfate is filtered, washed, ignited, and weighed. It has also been suggested to precipitate sulfate as strontium sulfate but the high solubility of the resulting salt renders the method of little value.

Fresenius (11) states that the

> . . . . exact estimation of sulfuric acid as barium sulfate is by no means so easy and simple as it was formerly supposed to be, but requires great care and attention. This is due to three causes: First, the barium sulfate is found to be far more soluble than was believed in solutions of free acids and of many salts; second, it is extremely likely to carry down with it foreign salts which are themselves soluble in water; third, when the precipitate has once separated in an impure state it is often very difficult to purify it completely.

The solution must contain only a little free hydrochloric acid and no nitric acid.

Kolthoff and Vogelenzang (26) claim that the solubility of barium sulfate is increased by a rise in temperature, by the presence of nitric acid, and to a lesser extent by hydrochloric acid, and that dry ignition in platinum causes large losses. Kato and Noda (24) obtained inexact results in the presence of equivalent solutions of sodium chloride, potassium chloride, and ammonium chloride, the potassium chloride giving the largest error. The error increased with the addition of alkali until the alkali chloride was present in the ratio of 2 mols to 1 of the sulfate. Sacher (40) found the barium sulfate much more soluble in potassium choride solution than in water, but his results do not confirm the interference of the chloride. De Sornay (9) found the usual method of determining sulfates to be inexact, particularly if much iron or aluminum were present. Krieble and Mangium (25) obtained concordant

results in the determination of sulfates in potassium sulfate in the presence of strong hydrochloric acid, although the results are slightly low. In the presence of sodium chloride and 2 cc. of concentrated hydrochloric acid added to 10 cc. of the potassium sulfate solution the results were high, but with a larger concentration of hydrochloric acid more nearly concordant results were found. Blumenthal and Guernsey (5) found that various strengths of acid did not influence the results to any great extent but that low acidity was preferable. Karaoglanow (21) found low results in the presence of nitric acid and large amounts of hydrochloric acid, while high results were obtained in the presence of potassium salts and ferric chloride.

The same worker (22) found that in dilute solution the precipitation of sulfuric acid as barium sulfate depends on the concentration of acid present and on the excess of barium chloride, the barium sulfate decreasing with the increase of barium chloride. The decrease is not due to the presence of barium chloride since barium sulfate is practically insoluble in it. High results were obtained in the presence of relatively large amounts of nitric acid and hydrochloric acid. Potassium chloride caused low results, but potassium nitrate high results. Potassium sulfate gave low results, but when hydrochloric acid was present the results were too high. The presence of potassium chloride and potassium sulfate together gave low results whether or not hydrochloric acid was present. The presence of sodium, ammonium, aluminum, and magnesium does not affect the results. Ferric chloride gives results much too low. However, in very dilute solutions containing hydrochloric acid the effect of iron is small.

Creighton (8) found aluminum to increase the weight of barium sulfate. De Sornay (9) found the determination of sulfate as barium sulfate inexact in the presence of iron and aluminum. The precipitation of sulfates as barium sulfate in the presence of iron salts yields a double sulfate of iron and barium which on ignition decomposes with a loss of sulfur trioxide (27, p. 275). Williams (47) obtained higher results in determining the sulfates in soil solutions when the iron and aluminum were removed than when they were left in. On account of their solvent action on barium sulfate the precipitate also is likely to become contaminated by the iron salts present.

The causes of these varying results have been variously explained. Ruppin (37) attributes the high results obtained to the occlusion of barium chloride and the low ones obtained under other conditions to the solubility of barium sulfate in the foreign salts present. Kolthoff and Vogelenzang (26) claim that the occlusion of barium chloride, the nitrates, calcium, iron, and potassium salts is chemical in nature and cannot be washed out after ignition as claimed by some. The error in the presence of phosphates is due to formation of barium phosphate. Kato and Noda (24) think the error caused by potassium is due to the fact that potassium sulfate and barium sulfate both crystallize in the same system and thus form mixed crystals. They favor the adsorption theory since the formula obtained for the ratio of salt to acid, and the percent-

age difference between the results obtained in the presence and in the absence of potassium chloride is very similar to the adsorption formula, it is therefore probable that the adsorption takes place during the precipitation of the barium sulfate. No such adsorption occurs in the presence of magnesium chloride.

According to Allen and Johnston (1) the solubility of barium sulfate is not greatly influenced by alkali salts, but the acidity is a more important factor. It is their opinion that adsorption is an important factor since barium chloride and "free" sulfuric acid are frequently identified as impurities in barium sulfate precipitates. Nitrates also are likely to be adsorbed, producing high results.

Blumenthal and Guernsey (5) found that there was little difference in the use of 5- and 10-per cent barium chloride added to solutions of constant volume and acidity, but the rate of adding it was somewhat more important. Phelps (33) claims that by precipitating in a hot neutral solution with barium chloride the contamination of the barium sulfate precipitate with foreign ions may be almost avoided and that the precipitate contaminated by ions such as potassium, sodium, and ammonium may be converted into barium sulfate by treatment with sulfuric acid, evaporation, and extraction of the alkali sulfate with water. Karaoglanow (23) obtained the best results when the barium chloride was added during a period of not less than 1.5 minutes, while Blumenthal and Guernsey (5) obtained the best results when the barium chloride was added at the rate of 5 cc. per minute. Allen and Johnston (1) recommend that the barium chloride be added to the hot sulfate solution at such a rate that 2 gm. of barium sulfate is precipitated in 3 to 6 minutes.

The error accruing in the determination of sulfates as barium sulfate may at times amount to 5 per cent of the whole (27, p. 277) and because of the time element involved in making many analyses, numerous volumetric methodshave been suggested. These in general, however, lack the accuracy of the gravimetric method (27, p. 277). Mohr (29) proposed to determine sulfuric acid by adding an excess of standard barium chloride and titrating the excess of barium chloride by means of standard sodium carbonate using phenolphthalein as indicator. This method is inaccurate (42, p. 311) in the presence of metals other than the alkalies or acid ions such as phosphates, carbonates, and oxalates which form insoluble salts with barium. Consequently it would be useless for the determination of sulfates in alkali soils.

Clemm (7) modified Mohr's method in that he precipitated the excess of barium chloride with standard sodium carbonate, filtered off the precipitated barium sulfate and carbonate, then titrated the excess of sodium carbonate with standard acid and from that calculated the sulfates present. This modification is open to the same objections as the original method. Bohlig (4) proposed a similar method in which he precipitated sulfate with barium carbonate, thereby forming an equivalent quantity of alkali carbonate which, after filtration, was estimated by means of standard acid. Here the presence of oxalates, arsenates, chromates, and phosphates is objectionable. Gross-

man (13) precipitated the sulfates with barium hydroxide, removed the excess of barium with carbon dioxide, thereby leaving an amount of alkali carbonate equivalent to the sulfates present, which was titrated with standard acid. This method is open to the same objections as Mohr's method. Augur and Gabillon (3) proposed to reduce the sulfuric acid and sulfates with hydriodic acid and to estimate the hydrogen sulfide liberated with standard iodine.

Rivett (35) precipitated sulfates as barium sulfate by the use of moist barium oxalate and estimated the amount of soluble oxalates set free with standard permanganate solution. Obviously, if there are metals present which form insoluble oxalates or acid ions which form insoluble barium compounds the results will be inaccurate.

The sulfates were determined by Marboutin and Moulinie (28) by precipitation with an excess of barium chloride, the excess being precipitated with potassium chromate and the excess potassium chromate titrated either with iodine or arsenious acid. An almost identical method was proposed by Telle (43) who used barium chloride, potassium dichromate, potassium iodide, and sodium thiosulfate solutions, titrating the liberated iodine with sodium thiosulfate. This latter method is very much like one proposed earlier by Hinman (15) and by Andrews (2), who precipitated the sulfates with a hydrochloric acid solution of barium chromate. The excess of barium chromate was removed by adding either ammonia or calcium carbonate to the boiling solution. The solution was then filtered and the alkali chromate present equivalent to the sulfuric acid, reduced with potassium iodide, the iodine liberated being titrated with standard thiosulfate. The barium chromate must be free from soluble chromates and must contain no soluble barium salt (44, p. 717) or barium carbonate.

Holliger (17) used the same method only varying the procedure slightly. Roemer (36) modified the method in that he titrated the alkali chromate resulting from the precipitation of the sulfate with ferrous ammonium sulfate using potassium ferric cyanide as an indicator. Komarowsky (20) applied the method, with modified manipulation, to the analysis of waters with good results. Ruys (38) applied it to the determination of alkali sulfates. North (32) modified the method in that he used standard solutions of barium chloride and potassium dichromate. He found it to be usable in the presence of the following ions: Si, K, Na, NH_4, Cr, Mg, Ca, Sr, Zn, Cd, Hg, Al, Ni, Co, Cl, PO_4, and B_4O_7. Sborgi and Sotgia (4) varied the procedure in that they used a standard solution of barium chloride and an unstandardized solution of potassium dichromate. Then by running two series and making a calculation they arrived at the sulfates present.

Wildenstein (46) and Repiton (34) precipitated the sulfate with standard barium chloride. The excess of barium is precipitated by standard potassium chromate, the potassium chromate itself forming the indicator. In applying this method (11, p. 438) to solutions containing the sulfates of magnesium, zinc, or cadmium, the sulfates are first dissolved in ammonia with the addition

of ammonium chloride heated with a little calcium chloride to remove any carbonate present, then the barium chloride is added, and finally the potassium chromate.

Edmunds (10) precipitated the sulfates with an excess of decinormal barium nitrate. The excess of barium is precipitated with potassium chromate and the excess of the latter then precipitated with an excess of decinormal silver nitrate. The excess of silver is determined in a portion of the filtrate.

Vaubel (45), followed by Müller (30), Müller and Durkes (31), and later by a large number of other workers, proposed to estimate sulfuric acid by means of benzidine hydrochloride. The sulfate is precipitated as benzidine sulfate which is filtered off, after which the acid set free is titrated in the filtrate by standard alkali.

According to Treadwell and Hall (44, p. 715) in this method there are two sources of error: first, the benzidine sulfate is not insoluble in water so that there is considerable sulfuric acid not precipitated, and second the precipitate tends to adsorb some benzidine hydrochloride. They influence the results of the analysis in opposite directions and neither wholly compensates for the other.

EXPERIMENTAL

A consideration of the various volumetric methods indicated that the chromate method was the most likely to give satisfactory results for the following reasons: First, it is easy of manipulation; second, the reagents are common and are not especially expensive; third, the end-point is sharp. The method is fairly rapid. A comparison has been made, therefore, of the barium sulfate gravimetric method and the chromate volumetric method on varying concentrations of sulfuric acid in pure solution. The effect of various salts likely to occur in natural soils also was considered. First a comparison was made of the volumetric and gravimetric methods in which the same quantity of sulfate was determined in solutions of varying concentrations. These results are given in table 1. Each result is the average of six closely agreeing determinations. In the actual work the sulfuric acid was determined in 10 cc. of each concentration. The results in the 1*N*, 0.5*N*, and 0.1*N* solutions have therefore been multiplied by 2, 4, and 20, respectively. Any error, therefore, made in the analysis is multiplied by these factors. The barium sulfate here, as elsewhere mentioned in this paper, was precipitated by adding the required amount of hot barium chloride drop by drop to the hot sulfate solution without stirring. The samples were digested for about two hours, usually left to stand over night, and filtered the next morning. The precipitates were washed with hot water until free of chloride as indicated by silver nitrate. The sulfates in the volumetric method were precipitated by adding a hydrochloric acid suspension of barium chromate until a drop of ammonium hydroxide indicated an excess of barium chromate. The solutions were kept near the boiling point for half an hour after which the excess of barium chromate was precipitated while

the solution was hot with concentrated ammonium hydroxide. The solution was cooled, made up to a definite volume without filtering and an aliquot part taken for analysis. No correction was made for the solubility of barium chromate since it is small and in the presence of the large excess of chromate ion would be very much smaller. The solubility of barium chromate in mol per liter at room temperature is 1.5×10–5 so that the solubility product is 2.3×10–10. If we have, say, 0.1*M* alkali chromate present which is 85 per cent ionized, the concentration of the barium ion would be only $2.7 \times 10-9$ mol per liter, and the concentration of the chromate ion coming from the barium chromate would be the same. This quantity may properly be neglected.

It is true that a small error would be introduced on account of the volume occupied by the precipitate, but this procedure was followed to avoid the washing of the precipitated barium sulfate and chromate as well as to avoid making the correction for the solubility of barium chromate under varying conditions, such as volume of filtrate and temperature.

TABLE 1

Sulfuric acid recovered from varying strengths of sulfuric acid by the barium sulfate gravimetric and the barium chromate volumetric methods

VOLUME OF H_2SO_4	APPROXIMATE STRENGTH	NUMBER OF ANALYSES MADE	H_2SO_4 RECOVERED	
			Gravimetric method	Volumetric method
cc.	*N*		*gm.*	*gm.*
10	2.0	6	1.0110	0.9899
20	1.0	6	1.0076	1.0038
40	0.5	6	1.0160	0.9258
200	0.1	6	1.0260	0.9110

If the sulfuric acid recovered by the barium sulfate method be taken as 100 per cent in each case, then the chromate method when applied to a 2*N* solution, yielded 97.9 per cent of the sulfuric acid present. From a normal solution 99.6 per cent was obtained, where as from the half normal and decinormal solutions respectively, 91.1 and 88.8 per cent of the acid was recovered. It seems, therefore, that the chromate method is best suited to solutions of about normal concentration. Acid of this concentration was used in this work.

THE EFFECT OF CHLORIDES

It is often desirable to determine sulfates in soil, water, and other material containing varying quantities of soluble salts. It is essential to know the influence of these salts upon the accuracy of the two methods.

Accordingly, varying quantities of approximately 2*N* solutions of the chlorides of sodium, potassium, aluminum, and ferric iron were added to 10 cc. solutions approximately normal sulfuric acid. The results are recorded in table 2. In each case these results are the average of three closely agreeing determinations.

TABLE 2

Sulfuric acid recovered in the presence of varying amounts and kinds of chlorides by the barium sulfate gravimetric and barium chromate volumetric methods*

STRENGTH OF CHLORIDE SOLUTION ADDED TO 10 CC. OF APPROXIMATELY NORMAL H_2SO_4	SULPHURIC ACID RECOVERED							
	Sodium chloride		Potassium chloride		Aluminum chloride		Ferric chloride	
	Gravimetric	Volumetric	Gravimetric	Volumetric	Gravimetric	Volumetric	Gravimetric	Volumetric
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm*
12.5 cc. 2*N* sol. + 2.5 cc. H_2O	0.5015	0.5048	0.4982	0.4940	0.5068	0.4805	0.5032	0.4174
10.0 cc. 2*N* sol. + 5.0 cc. H_2O	0.5012	0.5041	0.4979	0.4987	0.5076	0.4834	0.5034	0.4589
7.5 cc. 2*N* sol. + 7.5 cc. H_2O	0.5010	0.5017	0.4978	0.4987	0.5046	0 4834	0.5024	0.4612
5.0 cc. 2*N* sol. + 10.0 cc. H_2O	0.5004	0.5017	0.4994	0.4953	0.5028	0 4918	0.5019	0.4612
2.5 cc. 2*N* sol. + 12.5 cc. H_2O	0.5015	0.4983	0.5004	0.4950	0.5028	0.4994	0.5020	0.4781
Average	0.5011	0.5021	0.4987	0.4963	0.5048	0.4877	0.5026	0.4550

* Sulfuric acid recovered from 10 cc. of untreated H_2SO_4: 0.5038 gm. by barium sulfate gravimetric method; 0.5019 gm. by barium chromate volumetric method.

Sodium chloride has but little effect. In most cases this effect was slightly depressing. The average of the five sets of determinations by the gravimetric method compared with that obtained with the pure solution, shows 0.5011 gm. of sulfuric acid as against 0.5038 gm. found in the latter case. We may assume, then, that sodium chloride in the concentrations used has a slightly depressing effect on the determination of sulfuric acid by the gravimetric method. The volumetric method when used on the same concentrations gave in most cases slightly high results, but the average of the five sets of results, 0.5021 gm. agrees almost exactly with that obtained on the pure solution.

Potassium in the form of chloride, in every concentration and in both methods, exerted a slightly greater depression than did sodium chloride. The averages show 0.5011 gm. of sulfuric acid in the presence of sodium chloride against 0.4987 gm. in the presence of potassium chloride by the gravimetric method, and 0.5021 gm. of sulfuric acid in the presence of sodium chloride against 0.4963 gm. in the presence of potassium chloride by the volumetric method.

Aluminum chloride exerted an opposite effect with the gravimetric method. This positive error is most pronounced in the higher concentrations and decreases to about normal in the lower ones. In the average there is a small positive departure from that obtained in pure solution. By the volumetric method, however, results were obtained which are just the reverse. All the values but one, 0.4994, are lower than any obtained in the presence of either sodium or potassium salts or pure solutions by either method. The discrepancy is most marked in the higher concentrations and as the amount of aluminum chloride decreases, the error grows smaller until in the lower concentrations almost the normal value is obtained.

The effect of ferric chloride was similar to that of aluminum chloride. So far as can be judged by the data obtained, these two ions have about the same effect on the barium sulfate method, but the iron causes much lower results with the volumetric method than the aluminum does.

The causes of these abnormal results have been investigated by many workers, among whom are Allen and Johnston (1) and Johnston and Adams (19). They find, in opposition to the work of some investigators, that whereas the solubility of barium sulfate is but slightly influenced by the presence of alkali chloride, the amount of alkali sulfate occluded by the barium sulfate particles is increased. This conclusion is drawn because there is present in the precipitate before ignition (*a*) chloride almost certainly barium chloride, (*b*) sodium sulfate and (*c*) sodium hydrogen sulfate. The amount of these substances they find present depends on first, the composition of the original solution, second, the method of precipitation and third the length of time between precipitation and filtration. A high acidity will tend to reduce the amount of alkali sulfate occluded with the precipitated barium sulfate but will have a greater solvent action. If the barium sulfate is precipitated rapidly and cold, the particles will be small, thus producing a maximum surface on

which the occlusion may take place. If a considerable time elapses between precipitation and filtration, the equilibrium between the solid and dissolved phases will result in recrystallization and a consequent smaller amount of alkali sulfate occluded.

Hulett and Duschak (18) think the abnormal values follow from the formation of complex salts, but Blumenthal and Guernsey (5) do not believe they are explained either by the complex salt or that normal and bisulfates are occluded.

THE EFFECT OF NITRATES

The effect of the nitrates of the same elements is much more marked both by the gravimetric and the volumetric methods. These results are recorded in table 3. In each case the same amount of sulfuric acid is used. The results are the average of three to six determinations. In some cases the duplicate samples did not agree closely. This, according to Allen and Johnston is due to the occlusion of nitrates the selective adsorption of which points to a solid solution.

Sodium nitrate increased the amount of sulfuric acid found. This increase became smaller as the amount of sodium nitrate decreased, but even in the lowest concentration used it was considerable. The abnormal value is more marked in the volumetric than in the gravimetric method, and this is to be anticipated since in the hydrochloric acid solution in which the iodine is titrated there would be liberated nitric acid which would serve to oxidize the iodide ion to free iodine. Potassium nitrate caused a much more pronounced error than did sodium nitrate. On the average, this influence was more marked with the gravimetric method. To obtain concordant results a close adherence to set conditions must be maintained, and even under the best conditions the results will be high. Aluminum nitrate also was found to exert a pronounced influence; it gave too high results with the gravimetric method, but iu most cases caused low results with the volumetric method. With ferric nitrates, the gravimetric results are very slightly lowered while volumetric results are very markedly depressed. Here, as with the other nitrates studied, the greatest errors either positive or negative occurred in the higher concentrations, the values approaching normal in the lower ones.

When the sulfates are precipitated as barium sulfate in the presence of iron, aluminum or chromium salts, the sulfates of these metals are occluded and on ignition decompose, liberating sulfur trioxide and produce low results. The magnitude of the error depends on the concentration of the original solution and on the rate at which the precipitation takes place, the occlusion being greater in the presence of nitrates than in the presence of chloride. The nitrates, however, not only greatly further the occlusion of sulfates but are themselves occluded. This causes large positive errors. According to Hulett and Duschak (18) positive errors are caused by the formation of complex salts containing nitrogen.

TABLE 3

Sulfuric acid recovered in the presence of varying amounts and kinds of nitrates by the barium sulfate gravimetric and the barium chromate volumetric methods*

STRENGTH OF NITRATE SOLUTION ADDED TO 10 CC. OF APPROXIMATELY NORMAL H_2SO_4	SULPHURIC ACID RECOVERED							
	Sodium nitrate		Potassium nitrate		Aluminum nitrate		Ferric nitrate	
	Gravimetric	Volumetric	Gravimetric	Volumetric	Gravimetric	Volumetric	Gravimetric	Volumetric
	gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
12.5 cc. 2*N* sol. + 2.5 cc. H_2O	0.5165	0 5213	0.5655	0.5634	0.5186	0.4852	0.5010	0.4550
10.0 cc. 2*N* sol. + 5.0 cc. H_2O	0.5143	0.5196	0.5560	0.5442	0.5182	0.4909	0.5028	0.4786
7.5 cc. 2*N* sol. + 7.5 cc. H_2O	0.5078	0.5172	0.5413	0.5408	0.5108	0.4983	0.5040	0.4915
5.0 cc. 2*N* sol. + 10.0 cc. H_2O	0.5113	0.5156	0.5286	0.5304	0.5111	0.5037		0.5027
2.5 cc. 2*N* sol. + 12.5 cc. H_2O	0.5096	0.5136	0.5220	0.5068	0.5034	0.5135		0.4960
Average	0.5119	0.5175	0.5427	0.5371	0.5124	0.4983	0.5026	0.4848

* Sulfuric acid recovered from 10 cc. of untreated H_2SO_4: 0.5038 gm. by barium sulfate gravimetric method; 0.5019 gm. by barium chromate volumetric method.

The ignited barium sulfate precipitated in the presence of ferric nitrate was invariably colored by the ferric oxide produced. An attempt was made to remove this colored material by washing and decantation with dilute hydrochloric acid. The results as shown in table 4 are the average of three determinations. Precipitation was made in the evening and filtration took place the next forenoon. The weight of the precipitate decreased but was still somewhat high in the presence of aluminum, and in the case of the iron they were still colored by the iron oxide although the results are low compared with the untreated sulfuric acid. No doubt part of the loss was due to the solvent action of hydrochloric acid on the barium sulfate.

Higher results than those given in table 4 were obtained when barium sulfate precipitated in the presence of iron salts was digested in dilute hydrochloric acid for 2 hours and filtered, as compared with those left to digest over night and filtered the following morning. In this case the barium sulfate recovered

TABLE 4

Effect of Hydrochloric acid digestion on precipitated barium sulphate

STRENGTH OF NITRATE SOLUTION ADDED TO 10 CC. APPROXIMATELY NORMAL H_2SO_4	BARIUM SULFATE RECOVERED			
	Aluminum	Nitrate	Ferric nitrate	
	Original weight	Weight after digestion with HCl	Original weight	Weight after digestion with HCl
	gm.	*gm.*	*gm.*	*gm.*
12.5 cc. 2*N* nitrate + 2.5 cc. H_2O	0.5086	0.5052	0.5042	0.4984
10.0 cc. 2*N* nitrate + 5.0 cc. H_2O	0.5084	0.5059	0.5046	0.4994
7.5 cc. 2*N* nitrate + 7.5 cc. H_2O	0.5078	0.5048	0.5042	0.4993
5.0 cc. 2*N* nitrate + 10.0 cc. H_2O	0.5084	0.5056		
2.5 cc. 2*N* nitrate + 12.5 cc. H_2O	0.5050	0.4997		

varied from 0.5225 gm. in the presence of 12.5 cc. of 2*N* solution of ferric chloride (total solution 50 cc.) to 0.5172 when 5 cc. of 2*N* ferric chloride was added. In the results reported in table 4 the greater time between precipitation and filtration has favored the more complete reaction between the occluded sulfates and the precipitating reagent. No doubt the recrystallization of the of the barium sulfate liberated part of the occluded materials. This positive effect of iron was observed also when the same quantity of ferric chloride was added to sulfuric acid of varying strengths.

Thus when 10 cc. of 2*N* ferric chloride was added to 10 cc. of approximately normal solution of sulfuric acid, 0.5168 gm. of sulfuric acid was obtained as against 0.5056 in the absence of iron. When approximately 2*N* sulfuric acid was substituted for the normal solution, 1.0185 and 1.0110 gm. respectively of sulfuric acid was recovered. In each case the total volume of solution was 50 cc.

More nearly correct results may be obtained by precipitating the iron and aluminum salts by the use of ammonium hydroxide and the sulfates as usual

with hot barium chloride. After the precipitation is complete the hydroxides are dissolved with 10 cc. of concentrated hydrochloric acid and the usual procedure followed. The results are recorded in table 5. Each chloride result is the average of three samples and each nitrate result the average from five to eight determinations.

By this procedure somewhat low results were obtained in the presence of ferric chloride, the average being 0.4911 gm. as against 0.4922 gm. in the pure solution. The concordance of samples, however was good as there was a maximum variation of 4 mgm. of barium sulfate between the highest and lowest in any set of three, and in no other set did it exceed 1.5 mgm.

When ferric nitrate was present, the average of eight determinations of sodium sulfate recovered was almost exactly the same as that obtained on the pure solution but there was a much larger variation between results than when

TABLE 5

Sodium sulfate recovered from 10 cc. of a solution of sodium sulfate treated with varying amounts of ferric and aluminum chlorides and nitrates*

SOLUTION			SODIUM SULFATE RECOVERED			
0.69 *N* Na_2SO_4	2 *N* salt	H_2O	Ferric chloride	Ferric nitrate	Aluminum chloride	Aluminum nitrate
cc.	*cc.*	*cc.*	*gm.*	*gm.*	*gm.*	*gm.*
10	12.5	2.5	0.4914	0.4920	0.4937	0.4992
10	10.0	5.0	0.4912	0.4911	0.4934	0.4965
10	7.5	7.5	0.4918	0.4925	0.4931	0.4957
10	5.0	10.0	0.4916	0.4927	0.4917	0.4938
10	2.5	12.5	0.4906	0.4920	0.4932	0.4936
Average.....			0.4911	0.4921	0.4930	0.4958

* The average of fifteen determinations showed that 10 cc. of the pure solution contained 0.4922 gm. of sodium sulfate.

the chloride was used In some cases the difference between the highest and lowest was as much as 13 mgm.

With aluminum chloride present, higher results were obtained than in the presence of ferric chloride. The concordance of samples however, was even better, the maximum difference being 3 mgm. of barium sulfate in any one set and in most cases less than 1 mgm. The average weight obtained, 0.4930 gm., was only slightly greater than that obtained from the pure solution and easily within experimental error.

When we turn to the study of aluminum nitrate we again observe that the nitrates caused higher results than chlorides. Here the average weight of sodium sulfate obtained in the presence of aluminum nitrate was 3.6 mgm. higher than that obtained on the pure solution. The concordance among samples was poor, the maximum difference was 7 mgm. in the presence of the maximum quantity of aluminum nitrate. It seems, however, that by this procedure more nearly accurate results are obtained.

THE EFFECT OF THE PASTEUR-CHAMBERLAND FILTER

The ultimate object of this work is the determination of sulfates in soil, particularly as applied to alkali soils. The first essential for such study is the preparation of a clear filtrate. In our work on the nitrates (12) and chlorides (16) clarifying agents, such as alum and lime, were used with excellent results. For obvious reasons, however, neither of these substances could be used for clarifying solutions in which sulfates were to be determined, particularly if there were any appreciable amounts of sulfate present as is the case with many alkali soils. It seemed then, that the only procedure was to clarify the solution with the Pasteur-Chamberland filter.

Before using the filters, it was desirable to know whether or not they adsorb the sulfates. Solutions of sodium sulfate, potassium sulfate, and magnesium sulfate were made up. Portions of these solutions were then filtered through new, unused filters which had previously been soaked in distilled water and

TABLE 6

Potassium sulfate and magnesium sulfate recovered from filtrates of potassium sulfate and magnesium sulfate from Pasteur-Chamberland filters

SALT USED	FIRST 10 CC.	SECOND 10 CC.	THIRD 10 CC.	FOURTH 10 CC.	FIFTH 10 CC.	SIXTH 10 CC.	10 CC. OF FILTRATE ABOVE 60 CC.	UNFILTERED PORTION
cc.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
K_2SO_4	0.3549	0.3519	0.3517	0.3519	0.3519	0.3520	0.3532	0.3523
$MgSO_4$	0.2921	0.2908	0.2902	0.2904	0.2911	0.2904	0.2889	0.2889
Na_2SO_4							0.4927	0.4931

then dried. The remaining portions were left unfiltered. Five filters were used, the sulfates being determined gravimetrically in the unfiltered and in successive six 10– cc. portions of the filtrate and also in that portion which came through the filter above 60 cc.

The first 10 cc. of the filtrate contains more potassium sulfate than the unfiltered part, this no doubt is due to the adsorptive action of the filter, for there is but 0.0004 gm. difference in 10 cc. in favor of the filtered samples. The average of the seven filtered samples is 0.35253 gm. of potassium sulfate in 10 cc. as against 0.3523 gm. in 10 cc. of the unfiltered, a difference of but 0.23 mgm. in 10 cc. of solution.

In the work with magnesium sulfate the first 60 cc. filtered gave a more concentrated solution. That portion above 60 cc. is identical with the unfiltered portion, namely, 0.2889 gm. of magnesium sulfate per 10 cc. of the solution. In the potassium sulfate solution the concentration occurred only in the first portion but the first six magnesium sulfate portions are all more concentrated than either the latter part of the filtrate or the unfiltered portion.

THE SOIL

The soil used was a brown loam obtained from Benson Ward, Utah. There was but little sulfate present; consequently, sodium and magnesium sulfate were added and the sulfate determined by leaching 25 gm. of the soil. After mixing the sulfates into the soil the mixture stood 3 days before analyzing. Portions of it were agitated with water in a mechanical shaker and later filtered through Pasteur-Chamberland filters, after which the sulfates were determined by the barium sulfate gravimetric and the chromate volumetric methods. These results are given in table 7 and are reported as percentages of sulfuric acid based on the air-dried soil.

TABLE 7

Sulfuric acid recovered from soil

SOIL TREATMENT	SULFURIC ACID RECOVERED			
	Sulfate gravimetric method	Chromate volumetric method	Ratio of sulfuric acid recovered by the volumetric chromate method as compared with the barium sulfate gravimetric method	
	per cent	*per cent*	*(vol.)*	*(grav.)*
Leaching	2.234	2.017	94.32 :	100
Agitation and filtration through Pasteur-Chamberland filter	2.266	2.187	96.52 :	100

RATIO OF SOIL TO WATER

The smallest ratio of soil to water which is necessary to extract the maximum quantity of sulfates from the soil was determined by preparing mixtures in which the ratio of soil to water was 1:5, 1:10, 1:15, and 1:20, respectively.

These mixtures were agitated in a mechanical shaker for 1 hour, then filtered through Pasteur-Chamberland filters. The sulfates were determined by both the chromate volumetric and the barium sulfate gravimetric methods. The results are recorded in table 8 which shows the percentages based on the air-dried soil of sulfates calculated to sulfuric acid recovered.

So far as this soil is concerned, containing as it does a mixture of about equal parts of sodium and magnesium sulfates, as great a quantity of sulfates is extracted from a mixture of the ratio of 1 part of soil to 5 parts of water as from mixtures of higher ratios. It is true that with the ratio of 1:15 the amount is somewhat higher, but this, it seems, must be due to experimental error since in the ratio 1:20 it falls back again to almost exactly the value it had in the 1:5 ratio. These slight variations may be due to unequal distribution of the sulfate in the soil, although the sulfates were finely pulverized and well mixed by spading them into the soil which was subsequently subjected to prolonged grinding and mixing in a ball mill.

TABLE 8

Sulfates calculated as sulfuric acid recovered from mixtures of soil and water in various ratios

RATIO	SULFURIC ACID RECOVERED		
	Gravimetric barium sulfate method	Chromate volumetric method	Ratio of sulfuric acid recovered by the volumetric chromate method as compared with the barium sulfate gravimetric method
	per cent	*per cent*	(*vol.*) : (*grav*)
1- 5	2.310	2.280	98.70 : 100
1-10	2.292	2.195	95.08 : 100
1-15	2.346	2.292	97.70 : 100
1-20	2.319	2.288	98.66 : 100

TIME OF SHAKING

Another question arose. How long must soil be agitated in order to obtain the maximum amount of sulfates possible with the ratio of soil to water used? In order to obtain some concrete data concerning the ordinary alkali soils, fifteen samples of the soil used in previous sections were made up in the ratio of 1 part of soil to 5 parts of water. Three of these samples were shaken 10 minutes, three 20 minutes, three 30 minutes, three 40 minutes, and three 50 minutes. The results are expressed in table 9.

TABLE 9

Percentages of sulfates, based on the air-dry soil and calculated as sulfuric acid, extracted by 5 parts of water to 1 part of soil and shaken for various lengths of time

TIME SHAKEN	BARIUM SULFATE GRAVIMETRIC METHOD	CHROMATE VOLUMETRIC METHOD	RATIO OF SULFURIC ACID RECOVERED BY THE VOLUMETRIC CHROMATE METHOD AS COMPARED WITH THE BARIUM SULFATE GRAVIMETRIC METHOD
min.	*per cent*	*per cent*	(*vol.*) : (*grav.*)
10	1.987	1.398	70.36 : 100
20	2.267	2.237	98.68 : 100
30	2.195	2.133	97.18 : 100
40	2.313	2.240	96.80 : 100
50	2.288	2.137	93.40 : 100

In our study of the nitrates (12) and chlorides (16) we found that nothing was to be gained by agitating the soil for more than 10 minutes but here equilibrium is not reached in that time, the maximum quantity being obtained after 40 minutes of agitation. This result was obtained from a solution not nearly saturated with the salt used. For example, at 0°, 100 gm. of water will dissolve 26.9 gm. of anhydrous magnesium sulfate, or 76.9 gm. of the heptahydrate, or 4.8 and 55.59 gm. of the corresponding salts of sodium. Under the present conditions there is present but 2.25 per cent of sulfates (about half sodium sulfate and half magnesium sulfate) calculated as sulfuric acid. Consequently, the solution does not approach saturation and yet the results show

that at least 40 minutes is necessary to reach equilibrium. If, as frequently happens, soils are rich in gypsum, then much longer shaking will be necessary to attain equilibrium in any ratio of soil to water that we wish to use.

It has been pointed out in the literature (27) that, in general, the volumetric methods for the determination of sulfates lack the accuracy of the barium sulfate gravimetric method. We found this to be true. Except in the presence of nitrates where nitric acid is liberated which oxidized part of the iodide present, consequently giving high results, the chromate volumetric method gives lower results than does the barium sulfate gravimetric method. The amount of this negative variation depends on the concentration of the solution. This may be observed by referring again to table 1. If the sulfuric acid obtained by the gravimetric barium sulfate method in each concentration is taken as 100 the volumetric chromate method is found to recover 97.92, 99.62, 91.13, and 88.80 per cent, respectively, from the $2N$, $1N$, $0.5N$ and $0.1N$ solutions of sulfuric acid.

The most nearly concordant results are obtained with solutions of about normal concentration. Here almost as much sulfuric acid is recovered by the chromate volumetric as by the barium sulfate gravimetric method. This ratio falls off as the concentration becomes either greater or smaller, the smallest percentage occurring in the $0.1N$ solution where only about 89 per cent of the sulfuric acid is recovered. It seems, therefore, that the volumetric chromate method is best suited to solutions of about normal concentrations. When the methods are applied to soil solutions more nearly concordant results under varying concentrations are obtained. This may be observed by referring to table 8 column 4. The sulfates recovered, calculated as sulfuric acid as determined by the volumetric method, vary from 98.7 per cent in the ratio 1:5 to 95.08 per cent in the ratio 1:10. But this decrease cannot be due to the difference in concentration since in the ratio 1:20, 98.66 per cent as much by this method as by the barium sulfate gravimetric method is recovered. This same variation is observed in the "determination of sulfates in the soil," by leaching and by agitation and filtration in which we obtained 94.32 and 96.52 per cent, respectively. In this leaching experiment it is probable that more organic matter is dissolved. In a chromic acid solution this would be oxidized and gives somewhat lower results.

In table 9 which gives data on the time of shaking, the recovery is shown to vary from 93.4 to 98.7 per cent. The volumetric chromate method gives as an average of all the results obtained on soil solutions 96.7 per cent as much sulfates calculated as sulfuric acid as does the gravimetric-barium sulfate method on the same solutions.

Since this method is considerably more rapid than the gravimetric method it seems that it might be used where a large number of sulfate determinations are to be made and a correction applied, depending upon the type of soil and the quantity of sulfates present.

SUMMARY

1. It requires a longer time of agitation to reach equilibrium in soil solution in which sulfates are to be determined than is necessary with chlorides (16) or nitrates (12). The time will depend on the kind and quantity of sulfates present.

2. The solution may be clarified by the use of either the filter or centrifuge. Lime or alum may not be used.

3. In the present case a ratio of 1 part of soil to 5 parts of water was all that was necessary for satisfactory extraction but this may vary greatly with different types of soil.

4. The chromate volumetric method recovers smaller quantities of sulfates than are obtained by the gravimetric method.

5. Since the chromate volumetric method is fairly rapid and easy of manipulation it may well be used for the determination of sulfates in soil solutions. Where the chromate volumetric method is used and a fair degree of accuracy is desired a factor must be used to correct for presence of aluminum, iron and nitrates.

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THE INFLUENCE OF MOISTURE AND SOLUBLE SALTS ON THE BACTERIAL ACTIVITIES OF THE SOIL

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In a previous article (1) we have shown that, in twenty-two soils varying widely in physical composition, maximum ammonification took place when the soil contained 60 per cent of its water-holding capacity as defined by Hilgard; nitrification was at a maximum when the soil contained between 50 and 60 per cent. Many of the soils showed two maxima for nitrogen fixation, viz., one, 50 to 60 per cent of total water-holding capacity and the other, 70 to 80 per cent. It is the purpose of this paper to consider the influence of various soluble salts upon the water requirements of the ammonifying and nitrifying organisms.

SOIL

The soil used in this work, taken from the college farm, is of a sedimentary nature. It was deposited by streams laden with debris from the near-by mountains which are composed largely of quartzite and limestone. A physical and chemical analysis of the soil, given in table 1, showed that it was a sandy loam very high in acid-soluble constitutents, but not excessively high in water-soluble constituents. The calcium and magnesium contents were very high and mainly in the form of the carbonate. The soil was well supplied with phosphorus and potassium and there was a fairly large quantity of iron present. In fact, all the elements of plant-food were present in abundance, except nitrogen which occurred in only small quantities. The soil was very productive and previous work had shown the ammonifying and nitrifying powers of the soil to be about the average for the soils of the arid regions. The nitrogen-fixing powers of the soil were above the average and previous work had shown it to have an intensely interesting bacterial flora.

The water-holding capacity of the soil, as determined by the Briggs' modification of the Hilgard (3) method, was 45 per cent. From 10 to 45 cc. of sterile water was added to the air-dried soil. This gave relatively the percentages of moisture stated in terms of water-holding capacity of the soil, that are listed in table 2 for the various determinations. However, there must have been a slight variation from set to set, depending upon the dryness of the soil used. This would shift the point of optimum either higher or lower as the case may be. Each entire set, however, was maintained at the same moisture content. Hence, they were directly comparable and varia-

tions within a set were due to the salts added and not to experimental errors. The various moisture contents which were used in the study are given in table 2.

TABLE 1

Physical and chemical composition of soil

PHYSICAL COMPOSITION		CHEMICAL COMPOSITION	
Constituent	Per cent	Constituent	Per cent
Coarse sand, above 1 mm.....	17.69	Insoluble matter.....	66.69
Fine sand, 1.0–0.03 mm.....	37.39	Potash (K_2O).....	0.55
Coarse silt, 0.03–0.01 mm.....	15.19	Soda (Na_2O).....	0.49
Medium silt, 0.01–0.003 mm.....	10.36	Lime (CaO).....	7.41
Fine silt, 0.003–0.001 mm.....	10.32	Magnesia (MgO).....	4.15
Clay below, 0.001 mm.....		Ferric oxide (Fe_2O_3).....	2.93
Moisture and loss.....	9.05	Alumina (Al_2O_3).....	3.49
		Phosphorus Pentoxide (P_2O_5).....	0.25
		Sulfur trioxide (SO_3).....	0.07
		Carbon dioxide (CO_2).....	7.62
		Humus.....	2.18
		Total nitrogen.....	0.15

TABLE 2

Approximate moisture contents at which ammonification and nitrification were tested

AMMONIFICATION		NITRIFICATION	
Moisture added	Moisture content in terms of moisture-holding capacity	Moisture added	Moisture content in terms of moisture-holding capacity.
per cent	*per cent*	*per cent*	*per cent*
45	100	35	77
40	88	30	66
35	77	25	55
30	66	20	44
25	55	15	33
20	44	10	22
15	33		
10	22		

METHOD OF EXPERIMENTATION

In order to determine the ammonifying power of the soil, 100-gm. portions of the soil, 2 gm. of dried blood, and quantities of various salts, as indicated in the several graphs, were weighed into sterile tumblers which were kept covered with petri dishes. The dried blood was thoroughly mixed with the soil by means of a sterile spatula and the water content made up to the desired 10 to 45 per cent in 5 per cent increments. The samples were incubated at 28°–30°C. for days and the ammonia determined by transferring the mixture with 400 cc. of distilled water to Kjedahl flasks adding 2 gm. of magnesium oxide and distilling into 0.1 *N* sulfuric acid.

The nitrifying power of the soils was determined in similar mixtures which were incubated for 21 days. The moisture content varied from 10 to 35 per cent and was restored every 7 days to the initial percentages. The nitric nitrogen was determined as follows (2):

The contents of the beaker, together with 500 cc. of distilled water and 2 gm. of alum, were placed in quart Mason jars and agitated for five minutes in a shaker.

An aliquot part (100 cc.) of the supernatant liquid was pipetted off, and, together with 2 cc. of a saturated solution of sodium hydroxide, was evaporated to about one-fourth of its original volume to free it from ammonia. To this were added 50 cc. of ammonia-free water, 5 gm. of "iron-by-hydrogen," and 30 cc. of sulfuric acid (sp. gr. 1.35). The neck of the reduction flask was fitted with a 2-hole stopper through which passed a 50-cc. separatory funnel and a bent tube which dipped into a vessel containing water in order to prevent mechanical loss. The acid was slowly added and allowed to stand until the rapid evolution of hydrogen was over. It was then heated to boiling for ten minutes. The contents of the side vessel were returned to the reduction flask before the reaction was complete, thus insuring the complete reduction of any nitrates which may have been carried over with the first violent evolution of the hydrogen. The contents of the reduction flask were transferred to Kjeldahl flasks, neutralized with sodium hydroxide, and distilled into standard acid. The excess of acid was titrated back with standard alkali, lacmoid being used as an indicator. Controls were run on all the reagents, including the alum used as a flocculent.

AMMONIFICATION

The results obtained in soils treated with the chloride, carbonate, sulfate, and nitrate of sodium are given in figure 1, as the averages of six or more closely agreeing determinations. Ammonification reached its maximum in soil containing 30 per cent of moisture in the case of chloride and carbonate, but in the case of the sulfate and nitrate maximum ammonification was reached at a moisture content 5 per cent higher. The relative toxicity of the various salts decreased as the percentage of water in the soil increased and was most pronounced in the soil treated with carbonate and least in that treated with nitrate. In the presence of sodium chloride and with 10 per cent of moisture there was only 67 per cent ammonia produced as compared with the untreated, whereas with 45 per cent of moisture there was 103 per cent ammonia produced as compared with the untreated soil. The relations between the other salt-treated soils and the check, considering the untreated as 100 per cent, were as follows:

Sodium carbonate	10 per cent of moisture,	53 per cent of ammonia
	45 per cent of moisture,	116 per cent of ammonia
Sodium sulfate	10 per cent of moisture,	53 per cent of ammonia
	45 per cent of moisture,	93 per cent of ammonia
Sodium nitrate	10 per cent of moisture,	32 per cent of ammonia
	45 per cent of moisture,	50 per cent of ammonia

This is what one would expect where the toxicity is due mainly to osmotic pressure, as is the case with these salts.

The results obtained for the chlorides, carbonates, sulfates, and nitrates of potassium are given in figure 2. The untreated soil, together with that receiving potassium nitrate and potassium carbonate, reached their maximum ammonifying efficiencies at a moisture content of 30 per cent, whereas the soils treated with sulfate, chloride, or nitrate reach their maximum at 35 per cent.

The relative toxicity of the different salts varied widely with the moisture content of the soil. Soil treated with potassium sulfate bore a nearly constant

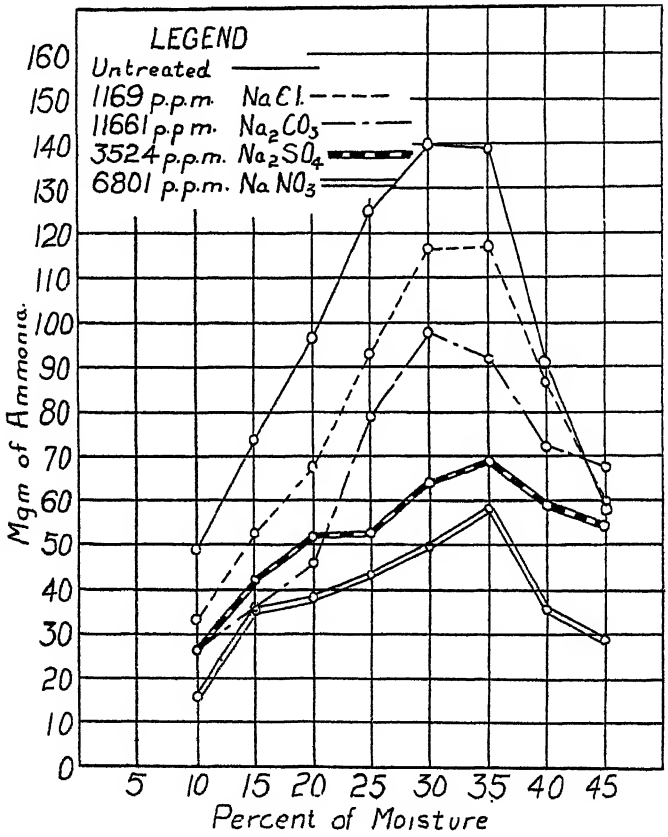

FIG. 1. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT SODIUM SALTS, AND VARYING PERCENTAGES OF WATER

relationship throughout to the untreated soil. The chloride and carbonate in soil with 10 per cent moisture decreased ammonification nearly 50 per cent, but with 45 per cent moisture the results became 91.8 and 142.0 per cent, respectively. In other words a sufficient quantity of potassium chloride in a soil with 10 per cent of moisture reduces ammonification about 50 per cent, but when the moisture content was raised to 35 per cent it had only a very slight retarding influence. With the carbonate the results were even more far-

reaching, for a quantity which, in a soil with low moisture content reduced ammonification 50 per cent, actually increased the relative quantity of ammonia produced when the moisture became excessive. These facts point strongly to the conclusion that in the case of potassium chloride and potassium carbonate the toxicity was due to osmotic effect, whereas in the case of potassium nitrate some physiological action must have occurred which was not offset by the mere dilution of the salt.

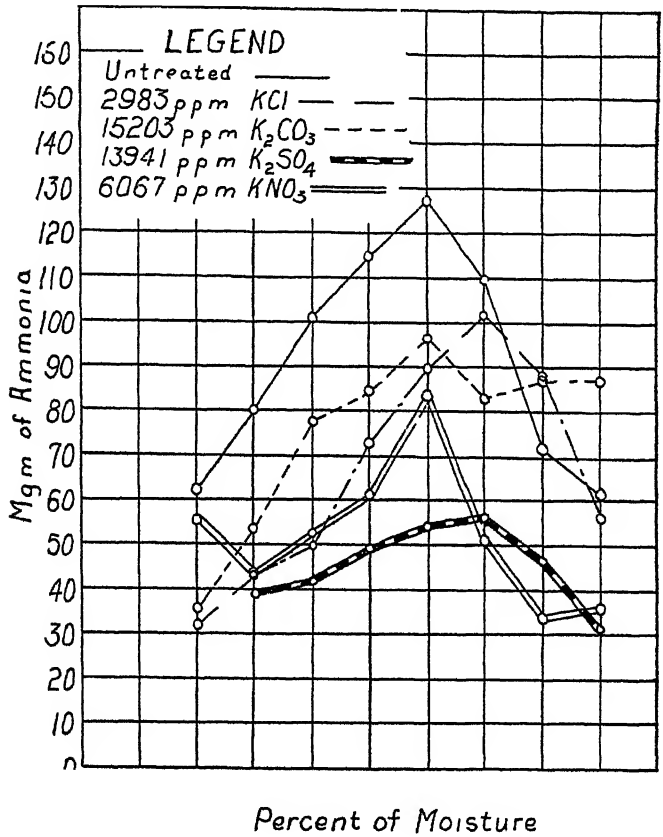

FIG. 2. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT POTASSIUM SALTS, AND VARYING PERCENTAGES OF WATER

The addition of chloride, carbonate, sulfate, or nitrate of calcium to a soil did not change the water requirements of that soil for optimum ammonification. This is shown in figure 3. The untreated and treated soils were all at their maximum ammonifying power at a moisture content of 30 per cent. There was no perceptible relative decrease in toxicity of these salts with increase of water-content. This is what one would expect if the toxicity is due to a change in the calcium-magnesium ratio. The same condition obtained

in the magnesium series (fig. 4). Both series bore out the conclusion that the calcium-magnesium ratio was an important factor. The nature of the cation, however, was an important factor, for the nitrate became relatively more toxic with increasing dilution both in the calcium and magnesium series. It has been quite evident throughout the consideration of all series that the nitrates were obeying a different law than were the chlorides, carbonates, and sulfates, and while the toxicity of the nitrate was due mainly to a chemical

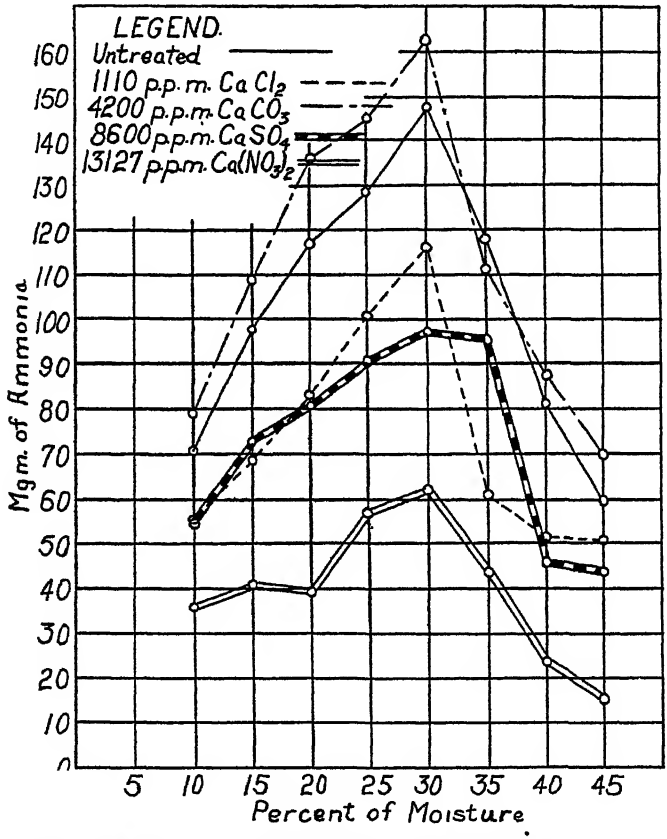

FIG. 3. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT CALCIUM SALTS, AND VARYING PERCENTAGES OF WATER

or physiological effect upon the protoplasm, the action of the chlorides, sulfates, and carbonates was due more largely to an osmotic effect. Magnesium carbonate becomes relatively less toxic with dilution, whereas the calcium carbonate becomes relatively more toxic. This is probably due to there being a preponderance of calcium in the soil, and the narrowing of the calcium-magnesium ratio makes it more nearly ideal for ammonification. The magnesium-sulfate-treated soil appears to require less moisture for optimum activity than do the soils receiving other salts.

So far in the discussion we have been comparing the action of compounds having the same electro-positive but various electro-negative ions. Hence, the results considered have given us an insight into the influence of the anions chloride, sulfate, nitrate, and carbonate upon the ammonifying efficiency of the soil. Soil samples were, therefore, treated with compounds in which the anion was a constant and the cation a variable. Figure 5 shows that results of treatment with chlorides. The addition of sodium chloride to the soil

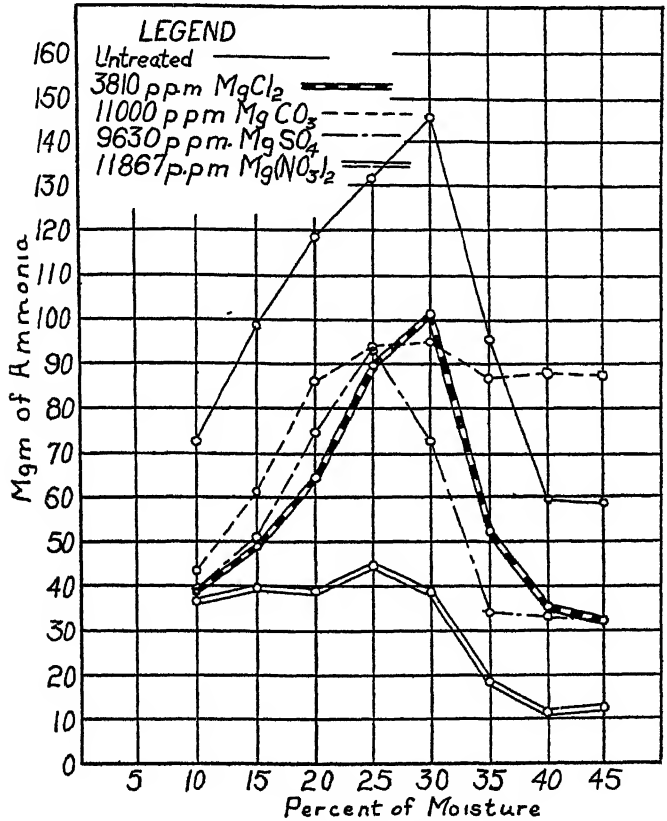

FIG. 4. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT MAGNESIUM SALTS AND VARYING PERCENTAGES OF WATER

shifted the point of maximum ammonification from 30 to 35 per cent content of moisture. In all the other soils, the point of maximum ammonification was at a moisture content of 30 per cent. The ratio of ammonia produced in the untreated soil to that produced in the salt-treated soil became narrower in the case of sodium and potassium chloride as the addition of water increased, whereas this ratio became greater with magnesium and calcium chloride. This increase of toxicity was very pronounced with calcium and indicated

that the calcium and magnesium ion added to this soil was a true poison to ammonifying bacteria. Potassium and sodium, however, acted more through the increasing of osmotic pressure in the soil and their relative effect was offset by the increasing of the water content.

The point of maximum ammonification with sodium nitrate, as with sodium, chloride, was raised 5 per cent, as shown in figure 6. Soil treated with magnesium nitrate reached its maximum ammonification when the water content

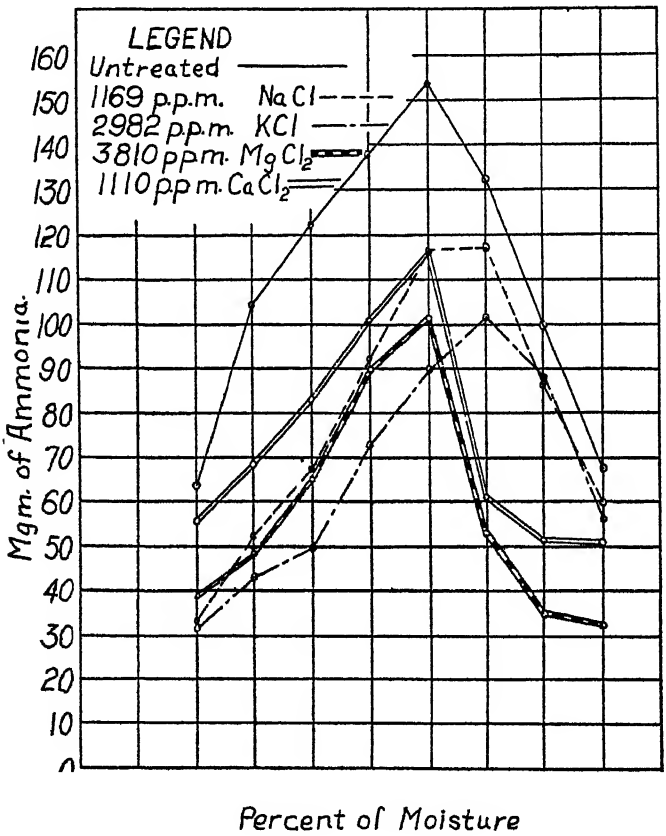

FIG. 5. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT CHLORIDES, AND VARYING PERCENTAGES OF WATER

of the soil was 25 per cent. The untreated soil, together with that receiving potassium and magnesium nitrate, reached its maximum at 25 per cent of water. As the quantity of water applied to the soil was increased, the ratio of ammonia produced in the untreated soil to that produced in the salt-treated soil increased in every case except that of sodium nitrate. Potassium nitrate-treated soil containing 10 per cent of water produced 86 per cent as much ammonia as the untreated soil, whereas with 45 per cent of water it produces

50 per cent; magnesium nitrate with 10 per cent of water produced 57 per cent as much ammonia and with 45 per cent of water, 22 per cent; calcium nitrate with 10 per cent of water produced 55 per cent as much ammonia and with 45 per cent of water, 30 per cent of ammonia. On the other hand, the sodium nitrate-treated soil receiving 10 per cent of water produced 24 per cent as much ammonia as the untreated soil and with 45 per cent of water, 50 per cent. In other words, the addition of water to a soil containing potassium, mag-

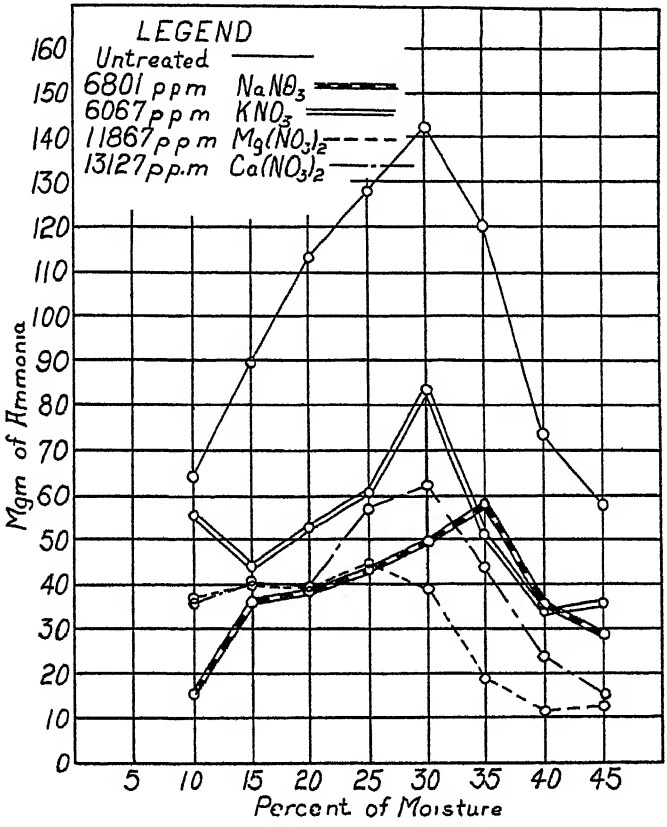

FIG. 6. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT NITRATES, AND VARYING PERCENTAGES OF WATER

nesium, or calcium nitrate increased the quantity of ammonia produced up to a certain maximum which lies between the moisture contents of 25 and 30 per cent. It decreased, however, the relative quantity of ammonia produced as compared with the untreated soil. This fact bears out the proposition that the toxic action of the nitrates was due in a large measure to a physiological effect upon the living protoplasm of the microörganisms of the soil and not to physical changes produced in the soil.

The results obtained with the sodium, potassium, magnesium, and calcium carbonate-treated soils as compared with the untreated soil are given in figure 7. In each soil its maximum ammonification was reached when the soil contained 30 per cent of water. However, the quantity of ammonia found in the different soils varies widely and at every concentration of water the calcium chloride-treated soil produced more ammonia than the untreated soil. The sodium carbonate-treated soil with a 10 per cent moisture content

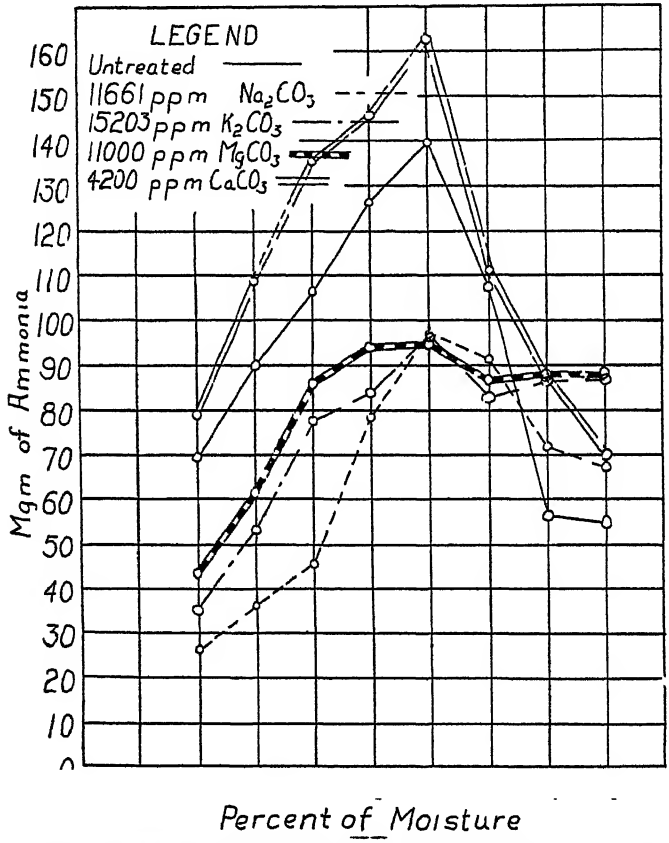

FIG. 7. CURVES OF AMMONIA PRODUCTION IN SOIL WITH AND WITHOUT CARBONATES, AND VARYING PERCENTAGES OF WATER

produced only 37.6 per cent as much ammonia as the untreated soil with a similar water content, whereas with 45 per cent of water the former produced 122.4 per cent as much as the latter. This indicated that the mere dilution of the carbonate decreased toxicity. The phenomenon appeared throughout the carbonate-treated soil, which is just the opposite to that occurring in the soils treated with chlorides and nitrates. This increase was real and not merely apparent, as would be the case if the nitrifying powers of the soil had decreased proportionately with the increased water content.

No such uniform effect was observed in the case of soil receiving sulfates, as is brought out in figure 8. The untreated soil and that receiving calcium sulfate reach their maximum ammonifying activity with a 30 per cent water content, whereas soil receiving sodium or potassium sulfate were not at their maximum efficiency until their moisture contents were raised to 35 per cent. This would seem to indicate that alkali soils containing sodium or potassium sulfate would be more productive with high than with low water content.

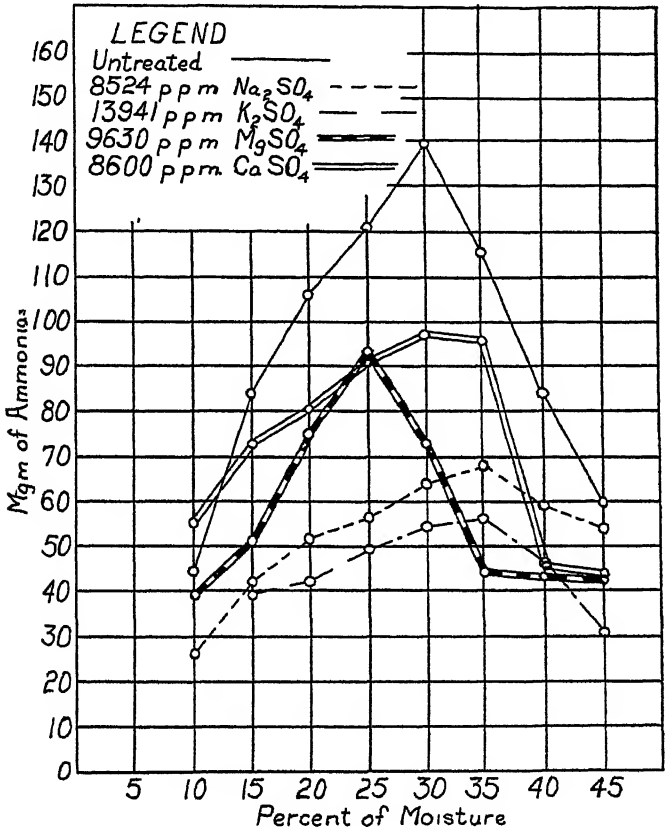

FIG. 8. CURVES OF AMMONIA PRODUCTION IN SOIL, WITH AND WITHOUT SULFATES, AND VARYING PERCENTAGES OF WATER

Soils containing magnesium sulfate were more productive of ammonia when the water content was only 25 per cent. The ratio of the amount of ammonia produced in the salt-treated soil to that produced in the untreated soil increased slightly with increased moisture content in soil treated with potassium sulfate and to a greater extent in soil treated with sodium sulfate. However, the ratio decreased in soil to which magnesium or calcium sulfate was added.

NITRIFICATION

The same soil with the same combinations of salts was tested for nitrifying powers. The results obtained with soil receiving chloride, carbonate, sulfate, and nitrate of sodium and with untreated soil is given in figure 9. On the ordinate is given the number of milligrams of nitric nitrogen produced in 100 grams of soil, whereas on the abscissa is given the percentage of water

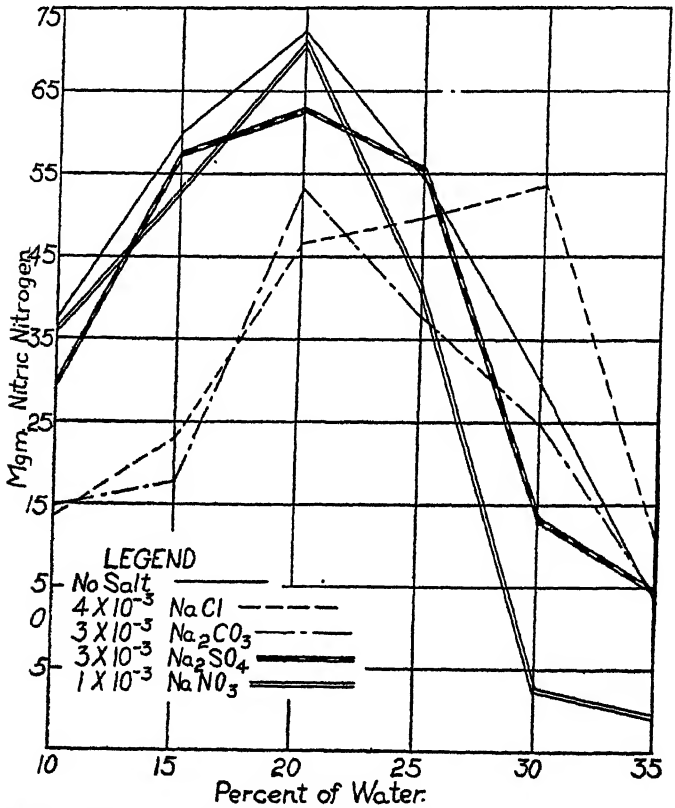

FIG. 9. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT SODIUM SALTS, AND VARYING PERCENTAGES OF WATER

applied to the air-dried soil. The soil reached its maximum nitrifying power when it received 20 per cent of water and lost it rapidly as the amount of water applied was increased. When the water-content reached 35 per cent nitrification practically ceased in all the tumblers except that receiving sodium chloride. In this there was an appreciable quantity of nitrates produced even at the highest water-content. Moreover, nitrification did not reach its maximum until this soil had received 30 per cent of water. Whether this was due to an actually increased nitrification or to a decreased synthetic

reaction is impossible to say. But inasmuch as the optimum moisture content for many of these changes was 30 per cent, it appeared probable that the causative factor was the latter. At a moisture-content of 30 or 35 per cent the nitrate-treated soil lost nitrates, but actual test showed that they did not lose nitrogen. In this case it was merely an acceleration of the synthetic reaction together with a slowing up of the nitrate produced. The proportion of nitrates found in the chloride-, carbonate-, and sulfate-treated soil increased

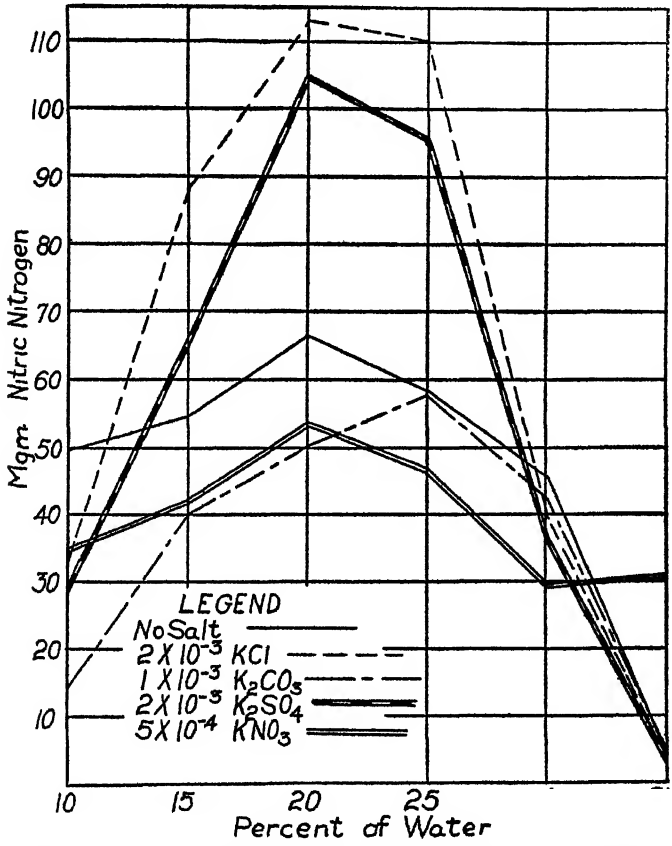

FIG. 10. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT POTASSIUM SALTS, AND VARYING PERCENTAGES OF WATER

as compared with the untreated soil, whereas that in nitrate-treated soil decreased with the increase of moisture-content.

This loss of nitrates did not appear in the case of potassium nitrate-treated soil (fig. 10) which lost no nitrates even when the soil contained 35 per cent of water. The potassium chloride-treated soil reached its maximum nitrifying efficiency when 25 per cent of water had been added to the soil,

whereas the untreated soil and those receiving the other potassium salts all reached their maximum activity at a moisture-content of 20 per cent of water. This was similar to the results obtained with the ammonifying series. The potassium chloride-treated soil required greater quantities of water for maximum ammonification than did the soils receiving the other salts. When the water content reached 35 per cent nitrification nearly ceased in all of the soils except that treated with potassium nitrate. The quantity of nitrates found

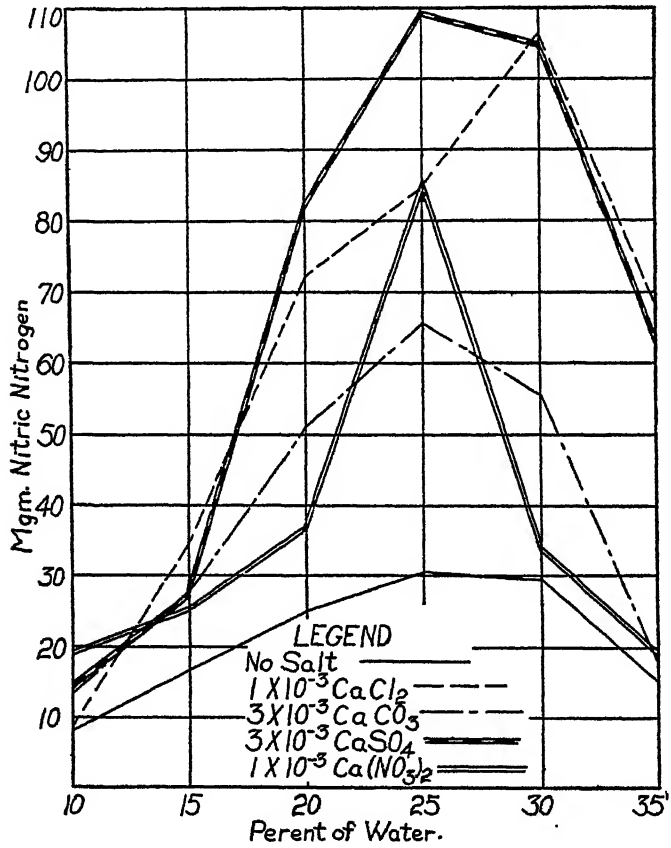

FIG. 11. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT SODIUM SALTS, AND VARYING PERCENTAGES OF WATER

in the chloride- and sulfate-treated soil increased relatively to the untreated soil as more water was applied, This increase was most pronounced at a content of 20 and 25 per cent of water. In soil containing 10 per cent of water both of these salts were toxic, but in soil containing 20 per cent of water there was found nearly twice as much nitric nitrogen as in the untreated soil. The treated and untreated soils produced practically the same quantities of nitric nitrogen at moisture-contents of 30 and 35 per cent. It was quite

evident from these results that the relative toxicity of these salts decreased as the water content of the soil increased, a condition to be looked for when the toxicity is an osmotic effect.

Soil treated with chloride of calcium, as was the case with the chloride of potassium and sodium, required more water for maximum nitrification than did those treated with the other salts (fig. 11). This would seem to indicate that the electro-negative ion is the controlling factor in the water re-

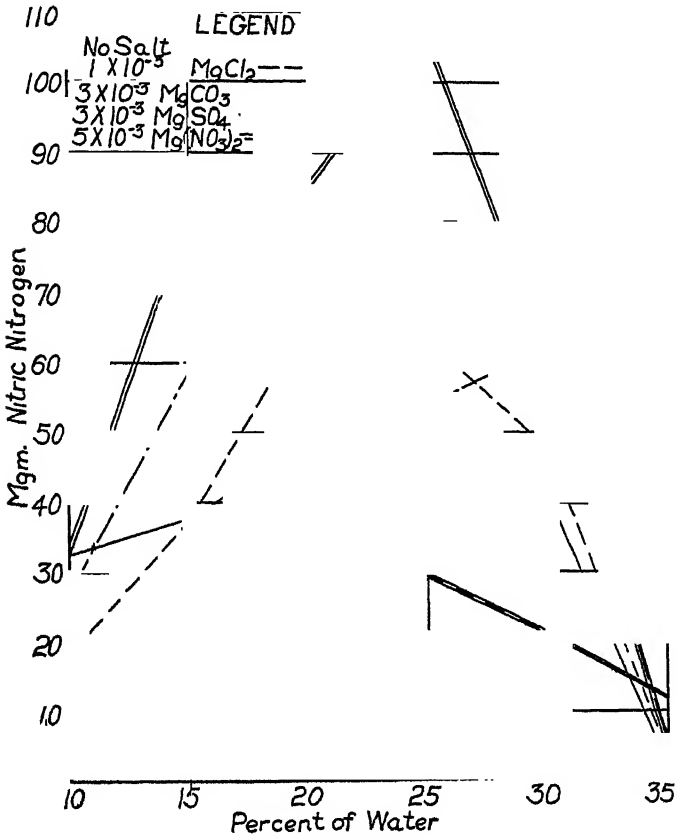

FIG. 12. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT MAGNESIUM SALTS, AND VARYING PERCENTAGES OF WATER

quirements of this class of organisms. The quantity of nitrates produced in the salt-treated soil was invariably higher than in the untreated soil, and this difference became greater in every case as the amount of water added to the soil was increased up to 25 per cent. This must have been due to a direct action of the salts upon the organism and not to a change in the calcium-magnesium ratio, for the same phenomenon appeared when magnesium salts were applied, (fig. 12). This soil already contained 7.41 per cent of

calcium oxide and 4.15 per cent of magnesium oxide, yet the addition of calcium and magnesium salts greatly increased the quantity of nitric nitrogen accumulated. This, however, may have been an apparent, not a real increase in nitrification, for all these salts decreased the quantity of ammonia found at unit time to a greater extent than they increased the nitrification. Hence, it is reasonable to conclude that the calcium and magnesium salts probably retard the action of the organisms found in the soil which utilizes nitrates.

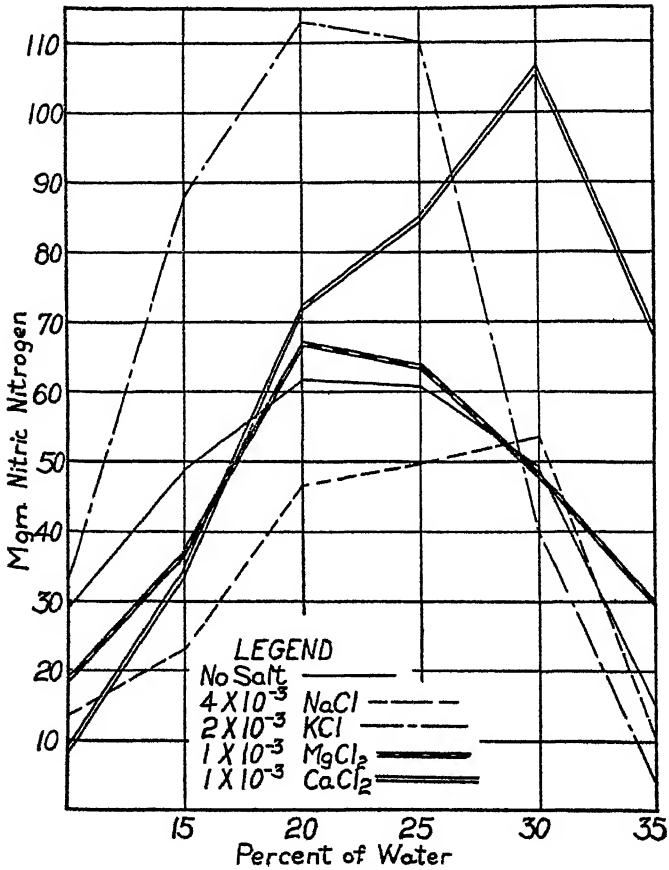

FIG. 13. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT CHLORIDES, AND VARYING PERCENTAGES OF WATER

The result of treating the soil with salts having a constant quantity of the electro-negative ion chlorine and a variable electro-positive ion are given in figure 13. Sodium chloride-and calcium chloride-treated soil reached their maximum nitrifying powers at a content of 30 per cent water, whereas potassium chloride-and magnesium chloride-treated soil reached their maximum at a content of 20 per cent water. This indicates a very marked influence on the part of the electro-positive ion. All of the salt-treated soils

at some water content were more efficient nitrifiers than the untreated soils. This is an important phenomenon, that a soil containing a certain salt may be toxic to nitrifying bacteria at one water-content but at a different water-content may become a favorable medium for these bacteria. This property is a characteristic of the various chlorides and is in keeping with what would be expected if the toxicity were due to osmotic influences.

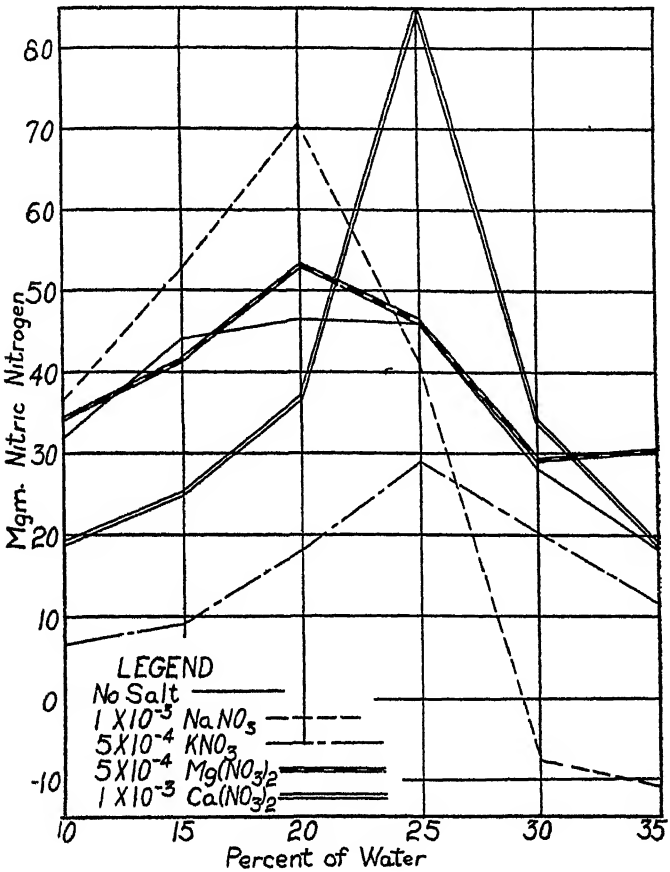

FIG. 14. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT NITRATES, AND VARYING PERCENTAGES OF WATER

This same phenomenon appeared in the case of the nitrates (fig. 14) and was very pronounced in soil which received calcium nitrate. When 1×10^{-3} mol of calcium nitrate were added to soil containing 10 per cent of water the nitrifying powers were decreased one-third, whereas this same quantity of calcium nitrate in soil containing 25 per cent of water nearly doubled the nitrification. Moreover, it is interesting to note that sodium nitrate was the only nitrate of those tested which, even in the presence of the highest content of

water, caused a loss of nitrates. It had repeatedly been our experience that treatment with sodium nitrates caused a disappearance of nitrates from soil, whereas potassium, calcium, and magnesium nitrate seldom caused a loss. Furthermore, we have experienced difficulty in inducing denitrification in our highly calcareous soils by the addition of nitrates, organic matter or water, either singly or in combination. At times there may be a disappearance of

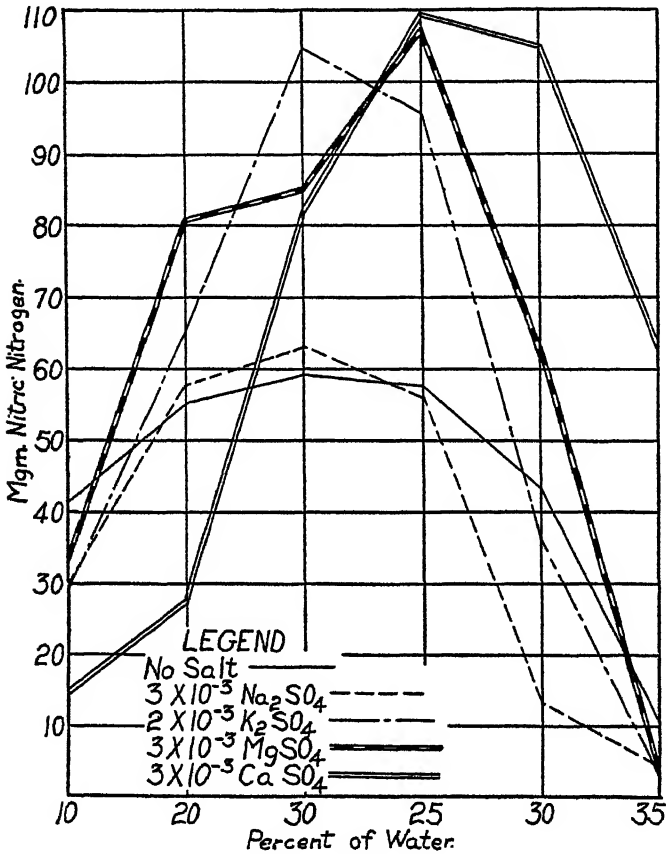

FIG. 15. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT SULFATES, AND VARYING PERCENTAGES OF WATER

nitrates, but an analysis of the soil for total nitrogen usually shows that it has been transformed into protein nitrogen.

This passage from a toxic to a stimulating medium by increased water content was very pronounced in the case of the sulfates (fig. 15). It is a well-known fact that in the spring when the water-content of the soil is high many plants can be started on alkali soil, but as the water evaporates the plants are killed. This is due in a great measure to the raising of salts from lower levels

by capillarity, but these results indicate that the mere removal of the water may play an important part in the killing of the plant. They indicate that the dilution of the salt content is important, as well as its removal by rains of winter and spring. This dilution influence was only slight in soil containing sodium sulfate but was very pronounced in soil containing potassium magnesium and calcium sulfate.

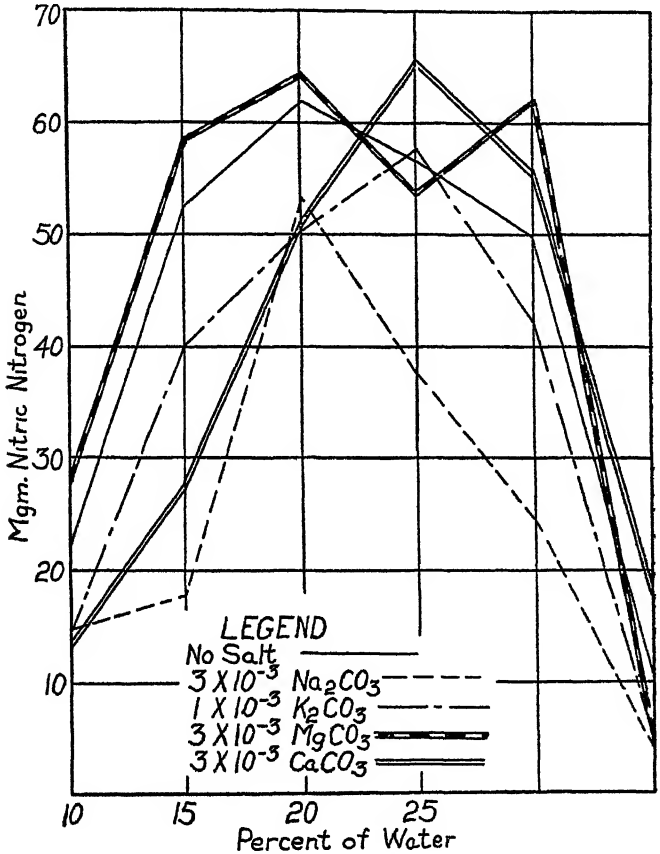

FIG. 16. CURVES OF NITRIC NITROGEN PRODUCTION IN SOIL, WITH AND WITHOUT CARBONATES, AND VARYING PERCENTAGES OF WATER

The influence of dilution by water was slight in soil treated with the carbonate (fig. 16). It did not appear at all in the case of sodium and potassium carbonate and was small with magnesium and calcium carbonate.

SUMMARY

The influence of the chlorides, nitrates, sulfates, and carbonates of sodium, potassium, magnesium, and calcium upon the moisture requirements of a

highly calcareous soil for bacterial activity was determined. The water-holding capacity of this soil (3) was 45 per cent.

Untreated soil, that receiving sodium carbonate, potassium carbonate, potassium nitrate, calcium carbonate, calcium sulfate, calcium nitrate, magnesium chloride and magnesium carbonate, had maximum ammonifying powers when the soil contained 30 per cent of water.

Soils containing sodium sulfate, sodium nitrate, potassium chloride and potassium sulfate possessed maximum ammonifying power at a water-content of 35 per cent, whereas when magnesium sulfate or magnesium nitrate were added to the same soil maximum ammonification occurred at a content of 25 per cent of water.

The relative toxicity of sodium chloride, sodium carbonate, potassium carbonate, and calcium carbonate, as measured in terms of ammonification, decreased as the amount of water added increased. All the other salts tested became relatively more toxic, thus indicating that in the case of these latter some other factor than osmotic pressure played a part.

Untreated soil, soil containing sodium carbonate, sodium sulfate, sodium nitrate, potassium chloride, potassium carbonate, potassium sulfate, potassium nitrate, magnesium chloride and magnesium carbonate, exerted their maximum nitrifying powers when the soil contained 20 per cent of water; whereas soil containing potassium carbonate, calcium sulfate, calcium nitrate, calcium carbonate, magnesium nitrate, and magnesium sulfate were at maximum nitrifying power when the soil contained 25 per cent of water. Soils containing sodium chloride and calcium chloride were at a maximum with 30 per cent of water.

The relative toxicity of various salts to the nitrifying organisms decreased as the amount of water added was increased.

The mere changing of the water content of a soil containing small quantities of potassium chloride, potassium sulfate, magnesium nitrate, and magnesium chloride may transform it from a toxic medium for nitrifiers to a strongly stimulating medium.

When 1×10^{-3} mol of sodium nitrate was added to 100 gm. of soil containing 35 per cent of water there was a loss of nitrates, but a similar quantity of calcium nitrate or even larger quantities of magnesium or potassium nitrate caused no loss of nitrates even in the presence of 35 per cent of water.

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EFFECT OF DIFFERENT REACTIONS ON THE GROWTH AND NODULE FORMATION OF SOYBEANS[1]

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Although it is well known that soil acidity and alkalinity have a marked effect on cultivated plants, especially certain legumes, yet, it has never been definitely determined at what reaction the legumes grow best and become inoculated most abundantly. Whether the favorable range of reaction is wide or narrow, and what this range is for each of the legumes are very important questions from both a practical and a scientific standpoint. In order to gain further information on these questions, the present investigation was undertaken.

The soybean was used in the beginning because of its adaptation to water cultures and because of its importance as a crop. Several different strains of soybean bacteria were studied. For comparison, some results with corn and cowpeas obtained under similar conditions are reported herein.

An exhaustive discussion of the literature on this subject does not seem necessary and only a brief review of some of the more important papers is given. The magnitude of the hydrogen- and hydroxyl- ion concentration of a number of soil solutions and suspensions have recently been determined by Gillespie (15), Sharp and Hoagland (35), Plummer (32), Truog (37), and others. These investigations have shown that soil solutions have a wide range of reactions, namely, from pH 3 to pH 9.

The importance of the effect of the soil reaction on the soil bacteria is well recognized. Gruzit (14) reported that an alkaline reaction was more favorable for the growth of the bacteria than an acid, or even neutral reaction. Salter (33) reported that red clover bacteria do best at a neutral or slightly acid reaction while the alfalfa bacteria do best at a slightly alkaline reaction. Fred and Loomis (11) reported that an alkaline reaction (pH 7.72) produced maximum growth of the alfalfa bacteria. Fred and Davenport (12) reported that a correlation exists between the acid resistance of the nodule bacteria and the

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The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Professors E. Truog and E. B. Fred under whose direction the work has been done.

acid resistance of the higher plants. Bewley and Hutchinson (2) reported that some of the legume bacteria are either killed in definitely acid soils, or at least lose their activity, while Hiltner (21) claimed that liming has an injurious effect on lupine bacteria.

The sensitiveness of plants to the reaction of dilute solutions of acids,bases and salts was noted by Kahlenberg and True (26), Heald (20) and Loew (29). These investigators studied primarily the direct chemical effect of reaction on seedlings and not the influence on growth, and hence did not use balanced nutrient solutions. Because of this condition definite conclusions can not be drawn from their data regarding influence on growth. Their data show, however, that seedlings differ widely in their behavior toward reaction.

Cameron and Breazeale (4) reported that corn was much more acid tolerant than wheat or clover. Hartwell and Pember (18) claimed that some of the cereals are more sensitive to acidity than others but no statement was made as to the relative sensitiveness. Hoagland (23) reported that barley seedlings grew better in a slighty acid reaction than in a neutral or alkaline reaction. This was also reported by Salter and McIlvane (34) in working with corn, wheat, soybeans and alfalfa. The data of the latter indicate that alfalfa is more sensitive to acidity than corn, wheat or soybeans. Joffe (25) reported that alfalfa produced good growth in soil cultures which were made very acid (pH 3.8) by the addition of sulfuric acid. Hixon (22) noted that there was a difference in water content, organic matter, and total ash in the roots of 16-day-old wheat seedlings grown at different reactions.

Hartwell and Pember (18) and Dachnowski (10) claimed that the hydrogen ion was more toxic to plant growth than the hydroxyl ion. This question was investigated by Hoagland (23) who reported the opposite results with barley seedlings. These contradictory results are possibly due to different methods of determining the reactions. Whether total acidity or hydrogen ion concentration is used as a criterion for indicating reactions is of great importance. Other factors, e. g., kind of nutrient solution used and proper maintenance of the desired reaction, are also important.

The change in reaction of the nutrient solution in contact with growing plant roots was noticed by Hartwell and Pember (18) who reported that an acid solution tended to become alkaline. This was also reported by Breazeale and LeClerc (3) who claimed from their work with wheat seedlings that the change in reaction of the nutrient solution was due to the selective absorption of the ions by the plants. The buffer condition of the nutrient solution and the frequency of renewing the solution are no doubt important factors in maintaining a constant reaction. The change in reaction of the nutrient solution in contact with plant roots during 1-day periods was found by Hoagland (23) to be quite considerable provided the initial reaction was not favorable.

Salter and McIlvane's (34) results indicate that their nutrient solution remained fairly constant over a period of 4 days when in contact with growing plants. Duggar (9) concluded that, in general, an acid or an alkaline

solution tended toward neutrality when in contact with growing plants. However, this change depended on the nutrient solution used and the rate of plant growth. The most favorable reaction also varied with the kind of nutrient solution used.

In connection with the influence of reaction on plant growth, it is well to mention the toxic effects of soluble aluminum salts as reported by several investigators. Abbott, Conner and Smalley (1) reported that the toxic effect of aluminum nitrate was about the same as a solution of nitric acid of equal normality; and that water extracts from acid soils containing soluble aluminum salts were as toxic to plant growth as a nutrient solution containing an equal amount of aluminum salts. Hartwell and Pember (19) found that aluminum salts were considerably more toxic to barley seedlings than to rye seedlings. The toxic effect of acidity alone was about the same on both plants. They concluded that lime may precipitate the aluminum and thus be of value in this way as well as in neutralizing the acidity. Mirasol (30) reported that aluminum salts which could be extracted from the soil with a solution of potassium nitrate were probably the cause of the unproductiveness of three acid soils of Illinois. Conner (6) reported that much of the harmful effects of acidity of soils is due to soluble aluminum salts; and the presence of abundant lime or phosphate will prevent this harmful effect. He noted that some plants are more sensitive to aluminum salts than others. This condition was also noted by Hartwell.

Undoubtedly, in very acid soils aluminum, manganese and other toxic substances go into solution and produce injurious effects on cultivated plants.

The results of the various investigations may be summarized as follows: The range of reaction of different soils is sufficiently wide to give conditions of acidity and alkalinity in some cases which are unfavorable to bacteria and higher plants. The different legume bacteria vary in their behavior toward reaction, and the degree of the acid resistance appears to be in the same direction as that of the host plants. In the case of plants, there are some contradictory results, but, in general, they indicate that plants differ in their behavior toward reaction. This is in line with field observations. In studying a problem of this nature, there are a number of factors which are difficult to control and the conflicting results obtained by the different investigators are perhaps due in part to the difficulty of controlling the reactions, and in some cases to the use of unfavorable nutrient solutions.

In regard to the toxic effects of soluble aluminum and other substances in acid soils, it appears that plants vary in their behavior toward these toxic substances and that the harmful effects of acidity in some soils are due in part to soluble aluminum salts.

GROWTH OF DIFFERENT STRAINS OF SOYBEAN BACTERIA AT VARIED REACTIONS

Since some investigators (2) had noted that many of the legume bacteria are either killed, or, at least rendered inactive in acid soils, it was thought best, as

a preliminary experiment, to determine the critical hydrogen- ion concentration of the various strains of soybean bacteria in pure cultures and also to determine if there is any marked difference in behavior of these strains of bacteria at different reactions. By strains of bacteria, is meant a pure culture isolated from a known variety of soybeans.

Twenty-one[2] strains of soybean bacteria were grown on mannit, on sucrose and on soil-extract agars. The mannit and sucrose agars were prepared according to Ashby's formula as follows:

Mannit or sucrose	15.0 gm.
$MgSO_4 \cdot 7H_2O$	0.2 gm.
KH_2PO_4	0.2 gm.
NaCl	0.2 gm.
$CaSO_4 \cdot 2H_2O$	0.1 gm.
Agar	15.0 gm.
Distilled water	1000.0 cc.

The soil extract agar was prepared by diluting 100 cc. of soil extract from a silt loam soil to 1000 cc. and adding 15 gm. each of mannit and agar. The range of reaction used was from pH 3.3 to pH 10 with the sucrose agar and from pH 3.3 to pH 7 with the mannit and soil extract agars. The desired reactions were obtained by adding varied amounts of sterile sulfuric acid and sodium hydroxide, as the case required, before the media were allowed to solidify in slants. The Clark and Lub's method for colorimetric determination of the reactions of solutions was employed. Each culture was inoculated with one drop of suspension containing the bacteria. Triplicates of each reaction were used in all cases. The cultures were incubated 15 to 20 days at 28°C. before final results were recorded.

In general the mannit and soil extract agars showed a more vigorous growth than the sucrose agar, although the three media showed only minor differences in critical pH for the various strains of bacteria. There were small differences in growth of bacteria between the reactions pH 7 and pH 6.5 but an increase in hydrogen-ion concentration from pH 6.5 to the critical concentration produced a gradual decrease in growth with each strain of bacteria. Eight strains of the bacteria were grown in the alkaline range, all of which grew at pH 10. The maximum growth of the eight strains grown in the alkaline range took place at reaction of about 7.6. Table 1 gives the critical hydrogen-ion concentration for the different strains of soybean bacteria studied. By critical hydrogen-ion concentration is meant the reaction at which the bacteria do not produce any visible growth during the 15 days after inoculation. It will be noted that there is not a great difference in the critical hydrogen-ion concentration for the various strains of soybean bacteria.

[2] Fourteen of the different strains of soybean bacteria studied were furnished through the kindness of the Bureau of Plant Industry, of the United States Department of Agriculture One strain was furnished through the kindness of Dr. A. L. Whiting, University of Illinois.

TABLE 1

The critical hydrogen-ion concentration for soybean bacteria on mannit, sucrose, and soil extract agar

STRAIN OF BACTERIA	NUMBER	CRITICAL pH VALUE
Arlington	118	4.2
Barchet	293	4.2
Barchet	218	4.6
Chinese	271	4.6
Cloud	270	4.2
Cornell	150	4.5
Haberlandt	210	4.0
Haberlandt	334	4.0
Hobta	337	4.0
Manchu	312	4.7
Manchu, Wisconsin Experiment Station	154	4.6
Medium early, Illinois Experiment Station		4.0
Mammoth yellow	338	4.2
Pingsu	275	4.2
Roosevelt	181	4.6
Roosevelt	187	4.0
Soybean	152	4.6
Taha	233	4.4
Tokio	256	4.6

PLANT CULTURES

Methods

The plants were grown in solution and sand cultures in the greenhouse from March 1 to July 25. The culture vessels used were 500 and 600-cc. percolators. These were provided with glass tubes and pinch-cocks at the bottom in order that the solutions might be easily removed without disturbing the plants. In the case of sand cultures, the percolators were supported by iron ring stands and wrapped in heavy brown paper to exclude the light. Those containing solution cultures of soybeans were placed in boxes and surrounded with moist sawdust to exclude light and prevent rapid changes of temperature. The glass tubes extended through holes in the boxes in order that the solutions might be removed readily. A few solution cultures of corn and cowpeas were also set up. For holding these percolators, circular holes were cut of such size in the top of a greenhouse bench that the percolators passed through to the rim around the mouth which acted as a support. The light was excluded from beneath the bench.

The most desirable nutrient solution for this type of investigation was unknown at the start. A modified form of Shive's three-salt solution was first used with the soybeans. The modification consisted in reducing the amount of $Ca(NO_3)_2$ to one-fourth that recommended by Shive, and adding an equal amount of $CaCl_2$. This made a total reduction of calcium to about one-half

that in the regular solution. The chloride was substituted for the nitrate, since large quantities of nitrates are known to hinder nodule formation. The reduction of calcium was made to reduce the precipitation of $Ca_3(PO_4)_2$ in the alkaline solutions. This modified solution proved unfavorable for nodule formation of soybeans in solution cultures. Shive's regular solution with varied amounts of nitrates was then tried, but again no nodules developed. Several other nutrient solutions, namely, Pfeffer's, Hopkins-Pettit's, Crone's, and also Mendota Lake water were tried with the result that only in Crone's nutrient solution and Mendota Lake water were nodules produced. Crone's solution being the most satisfactory, was chosen with slight modification for the work reported herein. The modification will be given later.

The reactions used in all cases were approximately pH 3, 4, 5, 6, 7, 8, 9 and 10. For specific reactions, see table 6. The Clark and Lub's method for colorimetric determination of reaction of solutions was employed in making the adjustments. The standards were checked at intervals with the hydrogen electrode. In order to maintain the reaction of the nutrient solution, in contact with plant roots, as constant as possible the solutions were renewed daily.

For the sand cultures, 20-mesh (Ottawa silica) sand was used. This was first thoroughly washed with distilled water. The sand was then placed in the percolators and washed with the respective solutions until the reaction remained constant on passing through the sand. The solution in sand cultures as in solution cultures were renewed daily. This was done by means of suction as sugested by McCall (31). The percolators were ideally adapted for changing of solutions.

The seeds were germinated in clean quartz sand and allowed to grow 3 to 5 days before being transferred to the percolators. Two seedlings were grown in each percolator both in sand and solution cultures. The seedlings, in case of the solution cultures, were held in place by means of paraffined corks and plugs of cotton. In order that the seedlings would not be subjected to a great change in reaction at once when being transferred to the percolators, the acid and alkaline reactions of the nutrient solution were brought to the desired points gradually over a period of 2 days. The solutions were inoculated 3 days after the seedlings had been transferred to the percolators. This was done by placing the inoculum in the nutrient solutions at the time the solutions were renewed. The plant cultures were grown for 25 to 35 days.

Growth of soybeans in Shive's nutrient solution at different reactions

As previously stated, a modified form of Shive's nutrient solution was first used in both sand and solution cultures. It was prepared from the following stock solutions in which the amounts of salts are indicated on the anhydrous basis.

(a) $CaCl_2$ ..... 50.0 gm.
$Ca(NO_3)_2$ ..... 50.0 gm.
Distilled water ..... 500.0 cc.

(b) $MgSO_4$ ..... 50.0 gm.
Distilled water ..... 500.0 cc.

(c) K_2HPO_4 ..... 50.0 gm.
Distilled water ..... 500.0 cc.

(d) $FeCl_3$ ..... 2.5 gm.
Distilled water ..... 300.0 cc.

Ten cubic centimeters of (a), (b), (c), and ten drops of (d) were added to 4 liters of distilled water. Dilute sulfuric acid or sodium hydroxide was added to portions of this solution until the desired reactions were obtained. The general method of procedure already outlined was followed. The plants were allowed to remain in the solution 24 days from time of inoculation.

TABLE 2

Growth and inoculation of soybeans in sand cultures with Shive's nutrient solution at different reactions

REACTION OF CULTURE	NODULES PER PLANT	PLANT DEVELOPMENT
pH		
3.2	0	Tops fair Roots dark and stubby
4.2	5	Roots better than at pH 3.2
5.0	12	Tops good Roots slightly dark
6.0	35	Tops good Roots good
6.9	49	Tops good Roots good
8.0	11	Tops good Roots slightly brown
9.0	2	Tops small Roots very brown
9.9	0	Very poor

The results of all plants in all experiments at different reactions will be referred to as at pH 3, 4, 5, 6, 7, 8, 9, and 10 although the actual pH value may have been slightly more or less. For specific reaction with Shive's nutrient solution, see table 2.

Only two nodules developed in Shive's nutrient solution and these appeared at pH 8. A poor and injured condition of the plants indicated that something was wrong with the nutrient solution. This may have been due to the presence of toxic impurities in the salts used. Plants at pH 3, 4 and 10 were almost

dead. Sand cultures of soybeans with Shive's nutrient solution were also carried on according to the regular method already described. The results of growth and inoculation with these are given in table 2. The best growth and inoculation were obtained at pH 6 and 7. In contrast to plants grown in solution cultures, the plants grown in sand cultures showed no injurious effect other than that due to reaction. The plants at pH 3, 4 and 10 had very dark roots and small tops. In general, a considerable increase in acidity or alkalinity caused a decrease in plant growth. Perhaps the absence of injurious effects in the sand cultures was due to adsorption of toxic substances from the solution by the sand.

The effect of nitrates on nodule formation in Shive's nutrient solution

Since practically no nodules developed in solution cultures with Shive's solution, it was thought that possibly the presence of nitrates prohibited inoculation. To determine the influence of nitrates on nodule formation, soybeans were grown in Shive's nutrient solutions containing 2, 1, $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ times the usual amount of nitrates recommended by Shive, and also in one solution entirely without nitrates.

For culture vessels, 500-cc. wide-mouthed bottles were used, and two soybean seedlings which had been germinated in clean quartz sand were placed in each. The seedlings were held in place with paraffined corks and plugs of cotton. The solutions were inoculated and renewed weekly. The plants were allowed to grow for four weeks, during which time not a single plant in any of the solutions developed any nodules. All the plants had yellowish leaves and somewhat dark and stubby roots indicating that the solution was toxic.

Influence of different nutrient solutions on nodule formation of soybeans

Since all attempts to get nodule formation on soybeans in solution cultures had practically failed, it was decided to determine the effects of different nutrient solutions on inoculation of soybeans. In addition to Shive's solution, Hopkin-Pettit's, Pfeffer's and Crone's solution, and also Mendota Lake water were used. The cultures were carried on in exactly the same manner as the previous ones. At the end of 4 weeks, the plants in Crone's nutrient solution and Mendota Lake water had developed a goodly number of nodules and the plant growth was healthy. Those in Shive's nutrient solution had developed only two nodules and the roots were dark and stubby, and those in the other two solutions did not develop any nodules at all. Their leaves were also yellowish and the roots dark. Plate 1 shows the root development and nodule formation in the different solutions.

Growth and inoculation of soybeans in Crone's nutrient solution at different reactions

The principal experiment on the influence of reaction on growth and inoculation of soybeans was next started with Crone's nutrient solution. The buffer condition of this solution was, however, unsatisfactory in the alkaline range and for this reason several different substances, namely, di-basic sodium phosphate, di-basic potassium phosphate, sodium glycero phosphate, and sodium carbonate and bicarbonate were added and tested for their buffer effect, and also influence on nodule formation. Of these, sodium carbonate at the rate of $\frac{3}{4}$ gm. per liter proved to be the most satisfactory, and hence was used. The salts for Crone's solution were ground to a fine powder and thoroughly mixed in the following proportions.

	gm.
KCl	100
$CaSO_4 \cdot 2H_2O$	25
$MgSO_4 \cdot 7H_2O$	25
$Ca_3(PO_4)_2$	25
$FePO_4$	25

For the solution, 12 gm. of this mixture were added to 8 liters of distilled water. The mixture was well shaken with the water and left to stand for one day, at end of which time the solution was filtered to remove the insoluble materials. The acid reactions were obtained by adding varied amounts of sulfuric acid. The alkaline reactions were obtained by first adding the sodium carbonate and then acid until the desired reaction existed.

The plants were grown in percolators according to the general method already outlined. Good plant growth took place at the favorable reactions. In all cases duplicates agreed as to nodule formation and root development. Plate 2 serves to indicate the relative size of plants and nodules per plants in solution cultures. It will be noted from plates 3 to 10, inclusive, that plants at pH 3, 4 and 10 had no nodules. Plants at pH 4.5 which is not given in figure 2 developed a few nodules, but at this reaction the roots were dark and stubby. Plants at pH 5 had fair inoculation. The tops of the plants at this reaction were as tall as those at pH 6, but were yellow and much less vigorous. Plants at pH 6 and 7 were decidedly the best, both as to growth and inoculation. Those at pH 6 were perhaps a trifle better than those at pH 7. Plants at pH 8 had some nodules but the roots were slightly brown. The roots at pH 9 and 10 were still browner and did not become inoculated. It should be noted that plants at pH 9 were a little taller than at pH 8, but of a very poor color. In all other cultures at pH 8 the plants were better than at pH 9. Table 3 gives dry weight of plants and number of nodules per plant.

The experiment just described was repeated using sand cultures according to general method already given. The same solution and reactions, were used as in the previous experiment. The extent of nodule formation was about the same as that in the solution cultures. The limits of nodule forma-

tion were pH 4 and 8. There was less injury from an unfavorable reaction at pH 3, 4, 5, 9 and 10 than in the solution cultures at these reactions. This was perhaps due to a smaller amount of nutrient solution actually in contact with the plant roots in the sand cultures than in the solution cultures, and hence a lesser amount of acid or alkali, making it easier for the plants to change the actual reaction to a more favorable one. Plate 13 gives the comparative growth in sand cultures.

TABLE 3

Growth and inoculation of soybeans in Crone's nutrient solution at different reactions

REACTION	DRY WEIGHT PER PLANT	NODULES PER PLANT	PLANT DEVELOPMENT
pH	*gm.*		
3.30	0.24	0	Tops dead Roots poor
3.97	0.40	0	Tops about dead Roots poor
4.95	1.00	30	Tops fair Roots dark and stubbed
6.50	1.42	77	Tops good Roots good
7.40	1.42	68	Tops good Roots good
8.20	1.15	21	Tops good Roots slightly brown
8.70	1.00	3	Tops fair Roots brown
9.60	0.60	0	Tops poor and yellow Roots very brown

Comparative growth of soybeans, corn and cowpeas at different reactions

For a comparison with the soybean, corn and cowpeas were grown in both solution and sand cultures with Crone's solution in exactly the same manner as the previous experiment with soybeans, except that nitrates instead of chlorides were used in the solutions for corn.

Plates 11, 12 and 14 serve to indicate the general growth which the corn and cowpeas made. The corn in the alkaline range of the solution cultures did not make good growth and the leaves were yellow. This was perhaps due to the lack of iron in solution, which was caused by precipitation under the alkaline conditions. The corn in the sand cultures grew better than in solution cultures and none of it became yellow. Corn plants at pH 5 in the sand cultures were inferior to the other plants at the beginning of the experiment and never grew as well as plants at pH 4. The maximum growth of corn took place at pH 6 and 7 in the sand cultures, and at pH 5 and 6 in the solution cultures. Plate 15 indicates that corn can grow at a considerably more

acid reaction than the cowpeas and soybeans. Apparently, as indicated in table 4 cowpeas have a wider range of inoculation than the soybeans. The corn was not grown in duplicate cultures and hence any conclusion with corn must be tentative.

TABLE 4

Growth and inoculation of cowpeas in sand cultures at different reactions

REACTION	NODULES PER PLANT	PLANT DEVELOPMENT
pH		
3.3	0	Tops fair Roots stubby and brown
3.97	20	Tops fair Roots slightly dark
4.95	22	Tops and roots good
6.5	32	Good plants, roots, and tops
7.4	33	Good plants, roots, and tops
8.2	26	Tops good Roots slightly brown
8.7	19	Tops fair Roots brown
9.6	14	Tops fair Roots very brown

The influence of the reaction of the culture medium on the reaction of the plant juices

The influence of the reaction of the culture medium on the reaction of the plant juices has been investigated by several workers (17, 38); and it was thought desirable to obtain additional information along this line. The reaction of the juices of the roots and leaves of some of the plants grown in the previous experiments was determined electrometrically by the method de-

TABLE 5

The reaction of the juices of plants grown in media of different reactions

REACTION OF MEDIA	SOYBEANS		COWPEAS		CORN	
	Leaves	Roots	Leaves	Roots	Leaves	Roots
pH	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
3.30	5.60	4.68	5.33	4.89	5.19	4.99
3.97	5.90	5.09	5.37	5.37	5.20	5.46
4.95	6.08	5.29	5.38	5.77	5.18	5.55
6.50	6.11	5.61	5.41	5.95	5.21	5.71
7.40	6.12	5.75	5.47	6.07	5.20	5.90
8.20	6.11	5.85	5.50	6.14	5.19	5.90
8.70	6.14	6.29	5.53	6.25	5.21	6.10
9.65	6.16	7.12	5.46	6.58	5.11	6.32

scribed by Clevenger (8) and Haas (17). The results are recorded in table 5. In general, the reactions of the plant juices as had previously been suggested (38) became more acid as the culture medium rose in acidity. The corn tops, however, showed no appreciable change. The reactions of the root juices were more nearly like those of the culture medium than were those of the leaves.

DISCUSSION

In making a comparison of the data presented, it should be clearly understood that pH 3 signifies an acidity ten times greater than pH 4, and pH 4 ten times greater than pH 5, etc. Hence, a small change in pH means a great difference in hydrogen-ion concentration. It will be noted from the data that the most favorable reaction for plant growth and nodule formation with soybean was from pH 6 to 7, which is a condition of slight acidity. This fact

TABLE 6

Change in reaction of Crone's nutrient solution in contact with soybean roots for 24 hours, as determined by the hydrogen electrode

CULTURE NUMBER	INITIAL REACTION	FINAL REACTION
	pH	*pH*
3	3.30	3.30
4	3.95	4.00
5	4.80	5.10
6	6.90	6.10
7	7.80	7.00
8	8.70	7.90
9	9.50	8.80
10	9.70	9.40

was indicated more clearly in the solution cultures than in the sand culture. The reactions at which maximum growth took place agrees with those reported by Hoagland (23) and Salter and McIlvane (34). Corn grew at a much stronger acidity than soybeans. This conforms with field observations.

The unsatisfactory results obtained in solution cultures with the modified form of Shive's nutrient solution are not readily explained since the plants grew well and became inoculated fairly well in the sand cultures. It was thought that possibly the salts used contained toxic substances which the sand adsorbed and thus prevented their toxic effect on the plants. In order to test this possibility some of the solution was thoroughly shaken with activated charcoal before being used. This appreciably lessened the injurious effects on the roots, but still no nodules appeared. Wilson (39) failed to obtain any nodules with soybeans in solution cultures using Pfeffer's nutrient solution even after varying the amount of nitrates. This same thing was found to be true with Shive's nutrient solution in the present investigation.

German and Didlake (13) reported inoculation of soybeans in solution cultures, using a nitrogen free commercial fertilizer for the nutrient salts. The writer believes that the unsatisfactory results obtained with Shive's nutrient solution in solution cultures were possibly due to toxic impurities in the salts used.

Crone's nutrient solution was not entirely satisfactory in the alkaline range because of the difficulty of maintaining a constant reaction when in contact with growing plants. This was even true to some extent after the addition of sodium carbonate as is indicated in table 6. The acid range was much more constant than the alkaline range, although it changed some. This same difficulty exists, of course, to some extent with all nutrient solutions, especially if the plants grow well in them.

The carbon dioxide excreted by the plant roots and that absorbed from the atmosphere were no doubt large factors in changing the reaction in the alkaline range.

It was found in the present investigation that when sodium glycero phosphate was added to Crone's solution the reaction remained almost constant for a daily period, but no nodules were formed in solution cultures. The addition of dibasic potassium phosphate to the alkaline range of Crone's solution was also found to hold the reaction of the solution fairly constant for daily periods, but nodule formation was again poor. In general, the reaction of a solution which was fairly favorable to plant growth so that considerable growth took place, would not remain constant very long in contact with the growing plants, unless the initial reaction of the solution was exactly the one most favorable for the plants. The change in reaction of the solution due to growing plants was always in the direction of a more favorable reaction. Salter and McIlvane's data (34) indicate that the reaction of their nutrient solution in contact with growing plants remained nearly constant during four-day periods. This was possibly due to the slow rate of growth of their plants.

The data show that pure cultures of soybean bacteria are able to grow at an acid reaction almost as great as that of the host plant. These results are not exactly in line with those of Bewley and Hutchinson (2) who reported that definitely acid soils would finally kill the nodule bacteria of lupines, red clover, and broad bean. However, they did not state the exact degree of acidity of the soil used and hence it is possible that they worked with very strongly acid soils. It will be seen from tables 2 and 3 that the best inoculation took place at a slightly acid to neutral reaction, although some inoculation took place at a reaction of pH 5 and even pH 4. The information secured thus far does not indicate that the critical hydrogen-ion concentration of pure cultures of the soybean bacteria is different from what it is in the soil.

The results show distinctly that the reaction of the media in which the soybeans are grown has a direct influence on growth and inoculation. The reactions which produced injury and poor inoculation were within the range of reactions of actual soil solutions and suspensions as reported by Gillespie

(15) Sharp and Hoagland (35), Plummer (32) Truog (37) and others. Different plants vary considerably in their ability to grow at reactions of pH 4, 5, and 6. Thus it will be seen that a proper adjustment of the reaction of the soil for different plants is of prime importance for the best growth and inoculation.

The reaction of the media in which the plants are grown often has a direct influence on the reaction of the plant juices. Further studies on the influence of reaction on legumes and legume bacteria are in progress.

SUMMARY

A study was made of the influence of acidity and alkalinity on growth and inoculation of soybeans in solution and sand cultures. The plants were grown in 500- and 600-cc. percolators. A modified form of Shive's nutrient solution was used at first, but with unsatisfactory results in solution cultures. Three other nutrient solutions were tested for influence on inoculation in solution cultures. Of these, Crone's nutrient solution proved to be the most satisfactory, and was selected with slight modification for the principal work reported herein. The reactions of the solutions were adjusted by adding varied amounts of acid or alkali as the case required. The reactions were kept as constant as possible by renewing the solutions daily. The old solutions were removed from the sand with suction before the new solutions were added. The cultures were allowed to grow from 25 to 35 days after inoculation. A few cultures of corn and cowpeas were grown under similar conditions to that of the soybean for comparison. Twenty-one different strains of soybean bacteria were grown on pure cultures of different reactions in order to compare the critical hydrogen-ion concentration of the soybean bacteria with that of the host plant.

1. Shive's nutrient solution was favorable for growth and inoculation of soybeans in sand cultures, but not in solution cultures. It seems possible that there were toxic impurities in the nutrient salts used which were adsorbed by the sand.

2. Crone's nutrient solution was favorable for growth and inoculation in both solution and sand cultures. The alkaline range of this solution has a very poor buffer action, which is improved markedly by the addition of $\frac{3}{4}$ gm. of sodium carbonate per liter.

3. The reaction of the nutrient solution in contact with growing plants does not remain constant very long, unless the initial reaction of the solution is the most favorable one for the plants. The rate of change in reaction is greater in the alkaline range than in the acid range. Plants growing rapidly apparently influence this rate of change more than slow growing plants.

4. The most favorable reaction for growth and inoculation of soybeans was pH 6.5. The limits for which inoculation took place were about pH 4.6 and 8. The limits for growth of soybeans were about pH 3.9 and 9.6. Reactions pH 4.95 and 8.2 are injurious to the growth of soybeans, but do not entirely prevent inoculation.

5. The hydrogen-ion concentrations which were markedly injurious to plant growth and inoculation in this investigation were not any greater and in some cases considerably less than the hydrogen-ion concentration of very acid soil solutions and suspensions as reported by recent investigators.

6. The critical hydrogen-ion concentration for nodule formation of soybeans was slightly less than that for plant growth. The different strains of soybean bacteria showed small differences in regard to critical hydrogen-ion concentration.

7. Corn grew at a greater acidity and alkalinity than the soybean or cowpea. The cowpea apparently has a greater range of reaction at which nodules are formed than the soybean.

8. The reaction of plant juices varied with the degree of acidity or alkalinity at which the plants were grown, except in the case of the juice of the corn leaves which showed little change. The juices of the roots followed the reaction of the media more closely than did the juices of the leaves.

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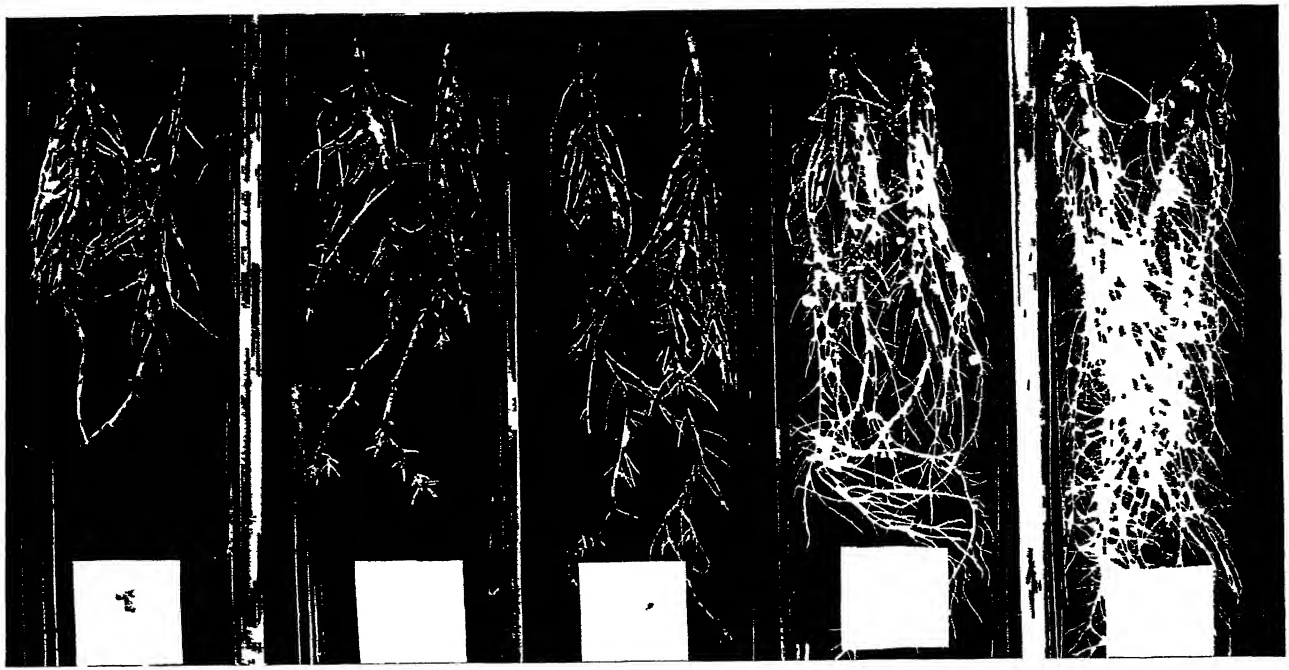
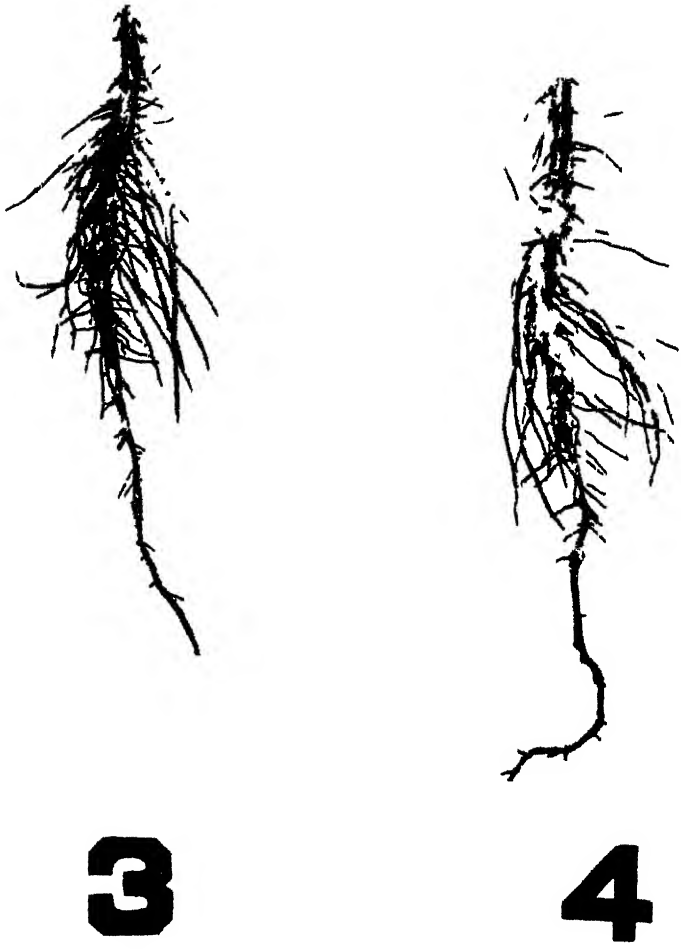


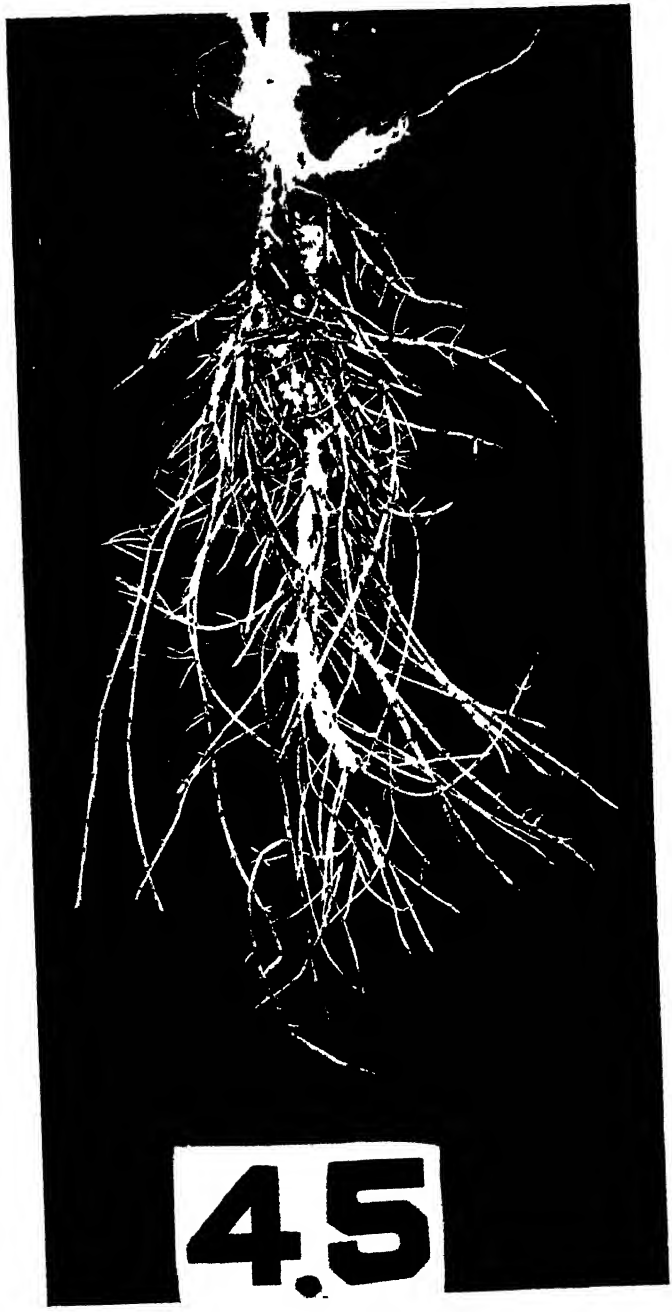
Shive's solution | Hopkin Pettit's solution | Pfeffer's solution | Crone's solution | Mendota lake water

THE ROOT GROWTH AND INOCULATION OF SOYBEANS IN DIFFERENT NUTRIENT SOLUTIONS

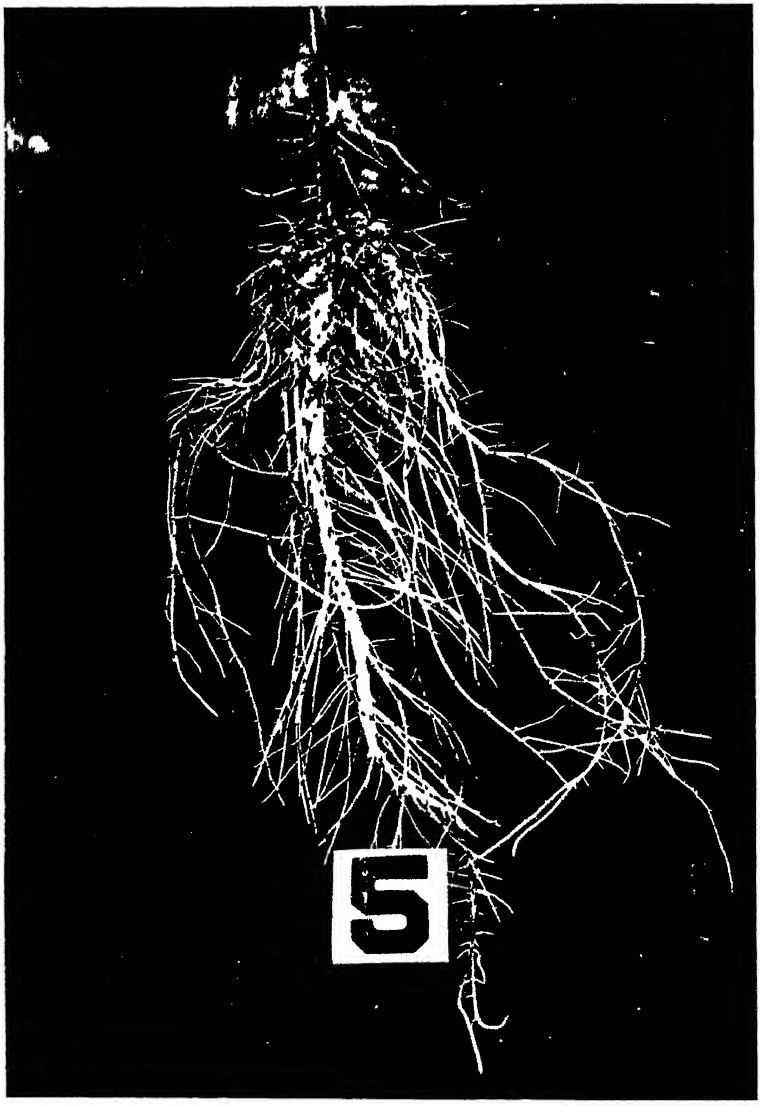
SOYBEANS GROWN IN SOLUTION CULTURES OF DIFFERENT REACTIONS. THE NUMBERS REPRESENT THE APPROXIMATE pH VALUES



SOYBEAN ROOTS GROWN IN SOLUTION CULTURES WITH pH VALUES OF APPROXIMATELY 3 AND 4



SOYBEAN ROOTS GROWN IN SOLUTION CULTURE WITH pH VALUE OF APPROXIMATELY 4.5



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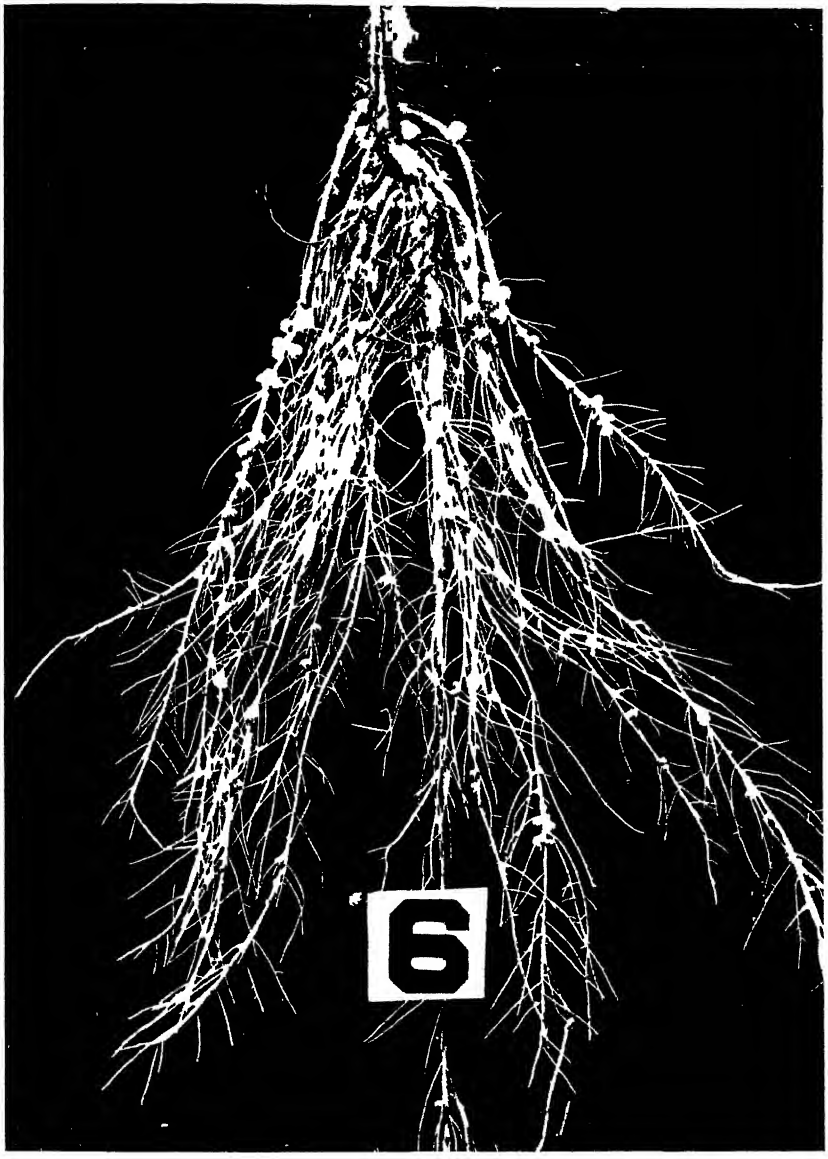

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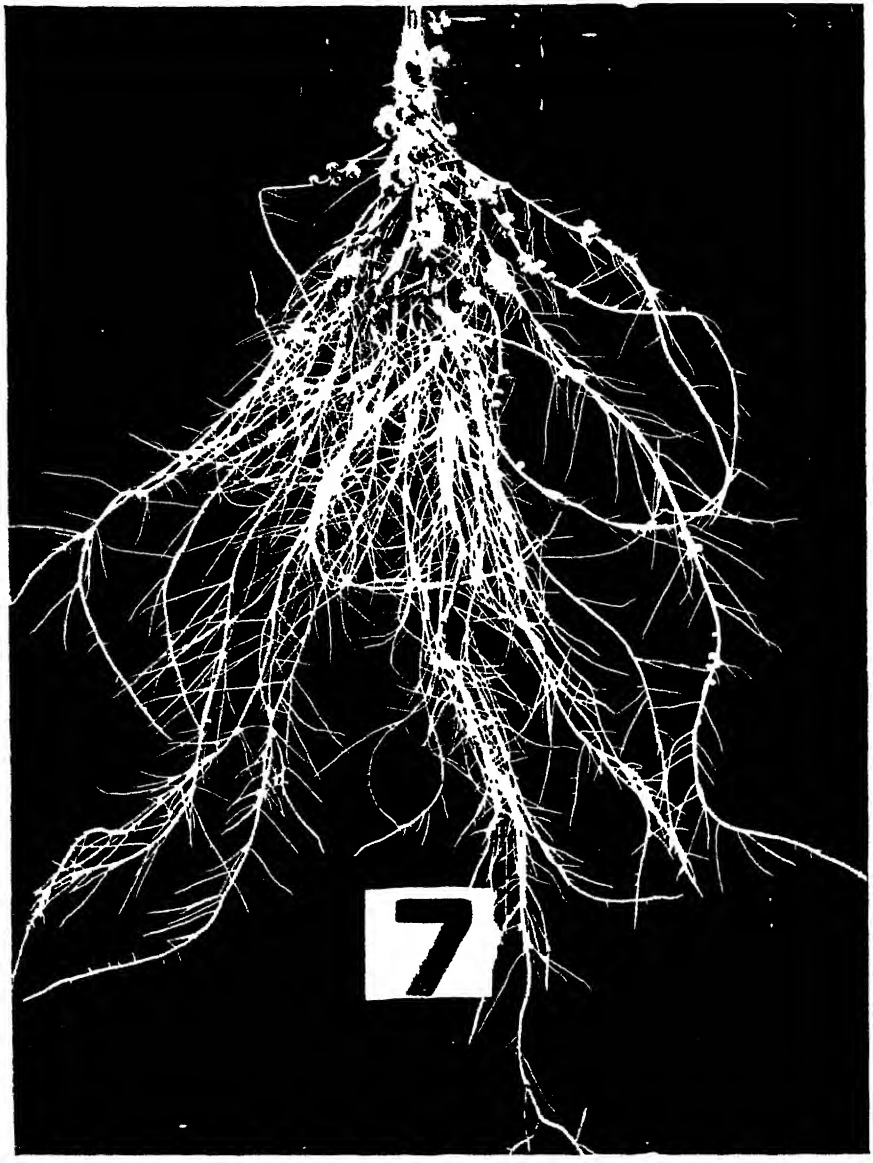

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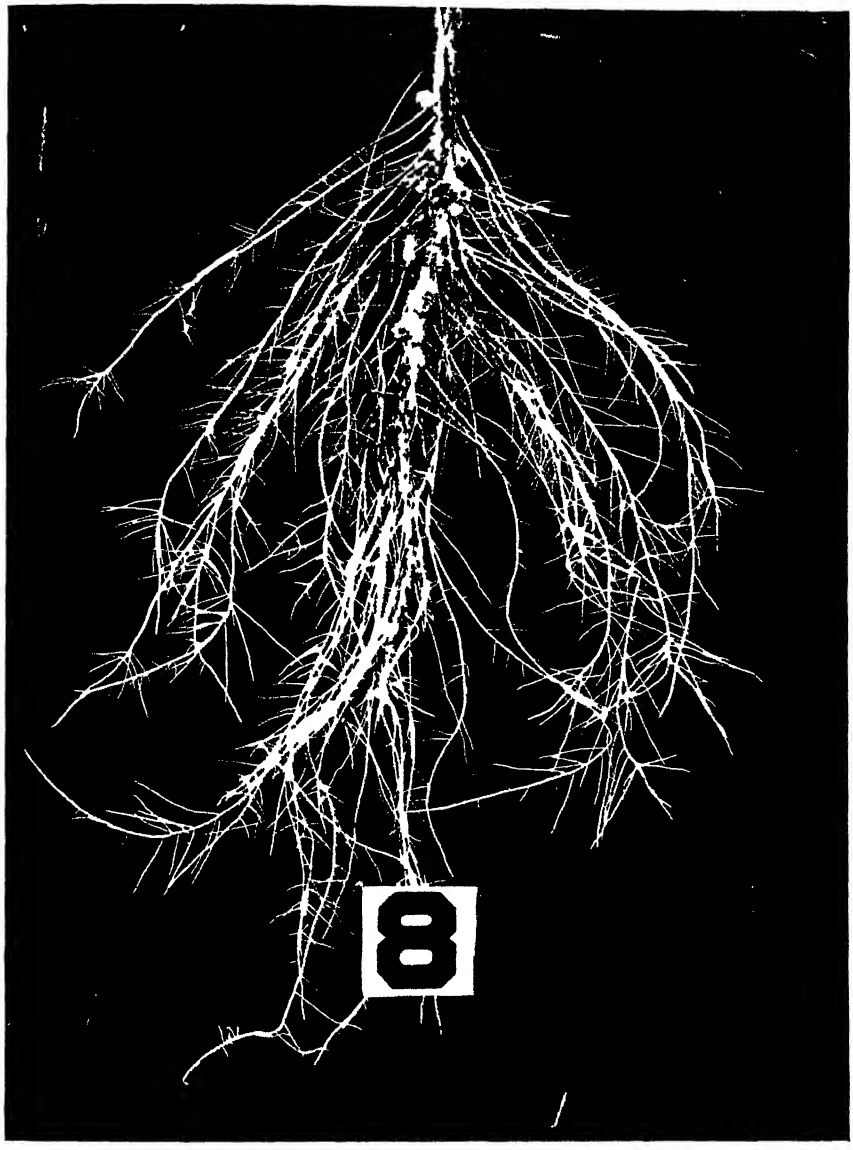

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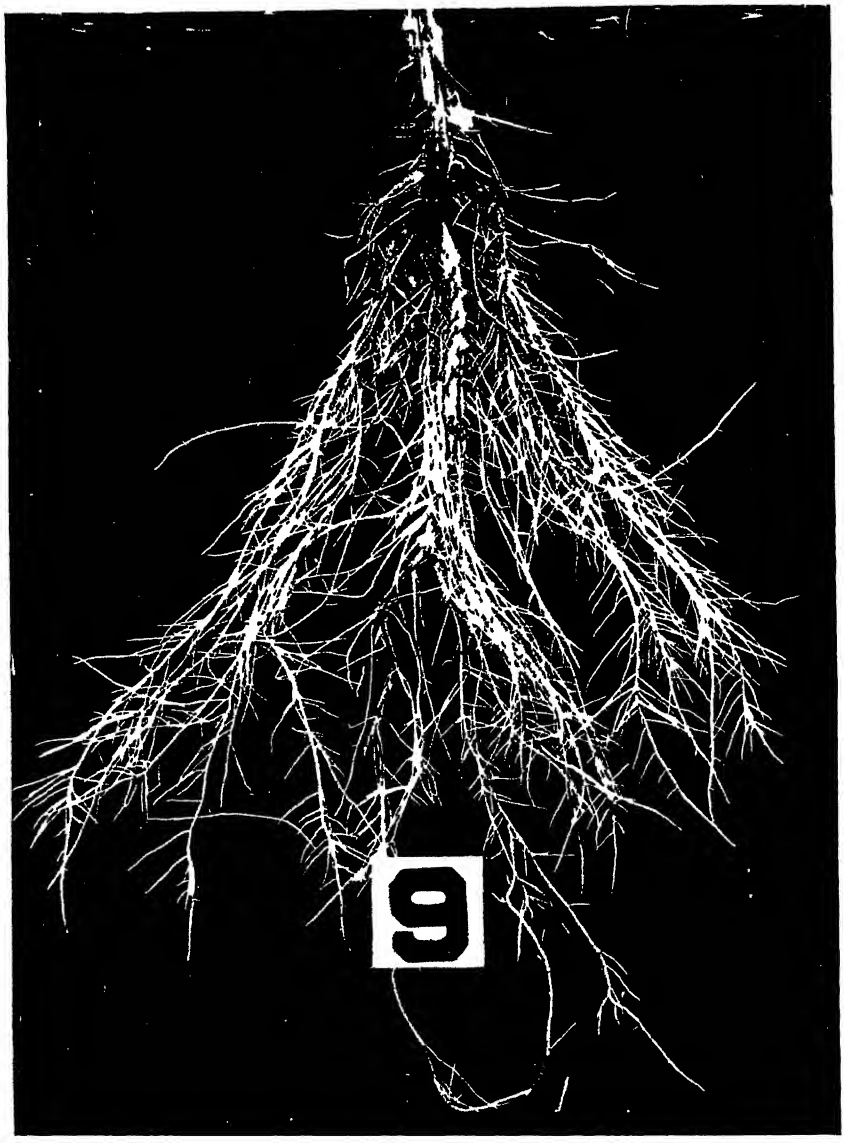

SOYBEAN ROOTS GROWN IN SOLUTION CULTURE WITH pH VALUE OF APPROXIMATELY 9

SOYBEAN ROOTS GROWN IN SOLUTION CULTURE WITH pH VALUE OF APPROXIMATELY 10

CORN GROWN IN SOLUTION CULTURES OF DIFFERENT REACTIONS THE NUMBERS GIVE THE APPROXIMATE pH VALUES OF THE CULTURES

CORN GROWN IN SAND CULTURES OF DIFFERENT REACTIONS. THE NUMBERS GIVE APPROXIMATE pH VALUES OF THE CULTURES

SOYBEANS GROWN IN SAND CULTURES OF DIFFERENT REACTIONS. THE NUMBERS GIVE APPROXIMATE pH VALUES OF THE CULTURES

COWPEAS GROWN IN SOLUTION CULTURES OF DIFFERENT REACTIONS THE NUMBERS GIVE APPROXIMATE pH VALUES OF THE CULTURES

CORN, SOYBEANS AND COWPEAS GROWN IN SOLUTION CULTURES OF APPROXIMATELY pH 4.0 IN EACH CASE

EFFECT OF TREE PRODUCTS ON BACTERIOLOGICAL ACTIVITIES IN SOIL: I. AMMONIFICATION AND NITRIFICATION

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INTRODUCTION

A large percentage of the soil in northern Idaho is a rather fine silt loam known technically as Helmer silt loam. This area is practically all in timber, but as the saw makes its inroads on the vast expanse of forest the acreage of land for agricultural purposes rapidly increases. This type of soil, apparently not markedly deficient in the essentials for plant growth, offers considerable difficulties when turned to agricultural use. The timber is usually removed *en masse* and the debris burned, thus the soil is cleared in the shortest possible time. It is then seeded to a suitable crop, such as clover, oats, wheat, or grass. Actual crop yields over a period of years are difficult to obtain, but it is the current opinion of those familiar with farming this area that the first crop yield on this type of soil is as good as could be expected considering the poor physical condition of the soil as the result of removing the timber. But each successive crop, in general, is poorer than the first even though the physical condition greatly improves with each crop. After three or four years better crops are obtained.

The fair yield obtained on the soil the first year after the removal of the timber is attributed to the small amount of readily available plant-food left in the soil. This readily available plant-food is removed in the first crop, and later crops are dependent upon the less available plant-food. The lack of productiveness for the next five to seven years is thought to be due to substances left in the soil by the timber which are deleterious to plant growth. The growing forest is thought to impart substances to the soil which are detrimental, and the accumulation of these products from year to year eventually results in a concentration which reacts upon the crop. These soils are known to the farmer and homesteader as "turpentine soils." The presence of turpentine has never been demonstrated, but it is thought that substances detrimental to plant growth exist in the soil as forest by-products, and that five to seven years of cropping is necessary to remove them.

REVIEW OF LITERATURE

A relatively small amount of information is available as to the effect of tree products on bacteriological activities in soil, and that much is more or less contradictory and does not

apply to Idaho conditions. The European forests which have been investigated relative to soil conditions are unlike our northwestern forests in that they contain variable amounts of humus material, somewhat peat-like, and have a very poor physical texture, while our forests are relatively free from peat and excessive amounts of organic matter, and have a good physical texture.

Baumann (1) states that it is not common to find nitrate in forest soils.

Boussingault (2) made a study of nitrate accumulation in forest soils and reported a very slight trace or none at all. His methods were later criticised by Weis (16).

Breal (3) tested the soils in beech forests at altitudes varying from 300 to 700 meters, and found only very slight traces of nitrate. He was of the opinion that nitrifying organisms formed only small amounts of nitrate, due to soil acidity, and the small amount formed was quickly removed by the luxuriant vegetation, which explained the absence of nitrate in the tests.

Ebermeyer (4) states that nitrifying organisms are not present in forest soils, due to their varying soil temperature and low moisture content.

Vogel von Falckenstein (5) found that light forest soils poor in lime produced but little nitrate, but that the amount formed was sufficient for the forest's demands. Forest soils not lacking in lime contained a larger amount of nitrate. Non-acid soils containing litter from pine and beech forests were able to gain in nitrate.

Grandeau (7) in a discussion based upon investigations by E. Henry, states that forest soils increase in nitrogen, but nitrification does not occur.

Hesselman (8), in a very extensive discourse on the forests of Denmark, states that the soils do not nitrify, and contain relatively no nitrogen as nitrate. The complete absence of nitrifying organisms was noted in many instances. The forests described by Hesselman contain a large amount of moss-like material over the soil, similar in some respects to our shallow peat. These conditions do not exist in the Idaho forests.

Koch (9) reported on studies of humus from pine and beech forest soils, and of the volatile oils and other products of conifers with reference to seed germination, the growth of plants, and the life and activity of yeasts and bacteria. Turpentine and carvene retarded the germination of corn, but had no marked effect after germination. Oil from the needles of silver pine was toxic. Ground pine needles added to the soil inhibited plant growth. Turpentine, resin, cedar oil, and various other products, exerted marked toxic action on nitrate formation from ammonium sulfate. These products also inhibited the development of yeasts in suitable media. The oxidation of ammonium sulfate was marked in beech humus, but small or negative in pine humus. He suggests that these substances may act as energy for the denitrifying group and thus prevent nitrate accumulation. He concluded that the majority of the substances tested were toxic to higher plants, yeasts, and bacteria, and that pine humus had a general unfavorable effect on plant growth. In later work (10) he tested the effect of colophony, resin, and tannin on biological transformations in soil. Pine resin acted as a source of energy for the nitrate reducing organisms, which he gave as an explanation of the low nitrate content of resinous soils. Resin was thought to hinder nitrification. Tannin was assimilated by molds and fungi, which caused a temporary loss of nitrate.

Migula (11) prepared decoctions of leaves and pine straw containing 0.5 per cent peptone and 0.5 per cent sugar. These were inoculated with soil and produced vigorous bacterial growth and acid formation. He attributes the decomposition of these substances in forest soil to the action of fungi. Surface layers of the soil contained few bacteria because of humus acids produced in the decomposition of the forest materials by fungi.

Moriya (12) analyzed the fallen leaves from various trees in forests, chiefly sugi (*Cryptomeria japonica*), akamatsu (*Pinus densiflora*), and kuramatsu (*Pinus thunbergii*). Some of the leaves contained as high as 0.9 per cent nitrogen. The soils bearing these forests were found to contain a high amount of nitrogen.

Muller and Weis (13) found that nitrification in beech humus was negligible unless treated with calcium carbonate, in which case it proceeded normally.

Parrozzoni (14) studied soils from forests of beech, cork oak, chestnut, and broom. Nitrate was found in all the soils except broom, while the highest amount was found in cork oak. Five soils were rich in nitrate and five were not.

Räuber (15) found ten to twenty times as many bacteria in calcareous forest soils as in sandy forest soils. There were very few organisms in the surface layer of soil due to the humic acids present from the decomposition of forest litter.

Weis (16) found nitrate in the soils of Denmark in amounts varying with the season. He states that nitrification in these soils is dependent upon the addition of lime. Soils under forest were found to contain as high as 65 mgm. of nitrate nitrogen per kilogram.

Zemplen and Roth (17) state that nitrogen is fixed by a hair-like growth on the forest trees, and the soil nitrogen supply is not only maintained but increased due to this fixation.

PURPOSE OF INVESTIGATION

Our aim in this investigation was to determine the presence or absence of substances in the various coniferous and deciduous trees, common to the Idaho forests, which are deleterious to bacteriological activities in soil. If such substances are present in the various trees, or arise from the decomposition of products from the trees, their accumulation from year to year would ultimately lead to an aggravated toxic condition in the soil. Fernow (6) states that an acre of forest produces 8,000 to 10,000 pounds of dry matter per year, of which half or more is wood above ground and 450 pounds is roots, leaving approximately 3,000 pounds of leaves per year. A forest 100 years of age would then have produced a total of 300,000 pounds of leaves, which is 15 pounds per 100 pounds of soil (acre 6 inches), or 15 per cent. It is, of course, impossible to estimate with accuracy the weight of needles which would fall on the soil from a given forest, and it would in all probability not be 15 per cent of the acre 6 inches of soil, but many leaves do fall, and to these are added the bark, twigs, cones, and other products, so that the actual weight of material entering the soil is no small amount. The undecomposed material representing the floor under the average forest may at times be several inches in thickness. The rainfall in this section of the northwest is never sufficient to wash away any appreciable amount of material comprising the forest floor, and leaching of products accumulating in the soil does not take place as in the mid-west and corn belt areas. In case these substances are detrimental to bacteriological activities in the soil, or their decomposition results in a toxic material, the soil would have ample opportunity to be heavily impregnated. This work was undertaken to determine if toxicity would develop as a result of applications of various forest materials to the soil, and the extent of this action. No attempt has been made to isolate material proving toxic. We have used various forest materials in amounts varying from 1 to 3 per cent. This is well below the amount we could expect to find in the soil naturally, based on the statements of Fernow.

EXPERIMENTAL DATA

Woods and tree products

The Idaho forests contain western red cedar (*Thuya plicata*), western white pine (*Pinus monticola*), western yellow pine (*Pinus ponderoso*), Douglas or red fir (*Pseudosuga taxifolio*), lowland or white fir (*Abies grandis*) and western larch (*Larix occidentalis*). White ash (*Frexinus americana*), and hard maple (*Acer saccharum*) were included in this work as representatives of the hard woods, but they are not common to the Idaho forests. Sawdust from kiln-dried boards made from all these timbers after the bark had been removed, was obtained, passed through a 10-mesh sieve, and then stored in paper bags in a dry room. These woods were used in varying amounts, as will be described later. After the work had progressed for some time, additional tree products were collected. These consisted of leaves, needles, cones, and bark from the above trees, and "forest floor" and fern brakes (*Pteris aquilina* L.). The needles were carefully trimmed from the twigs, air-dried, finely ground, and used in the same amounts as the other materials. The fern brakes were likewise treated. They were collected because it is well known that they are abundant on cut-over land, and are also quite poisonous if eaten in any considerable quantity. They can have no economic importance in this work but are included as a matter of interest. The "forest floor" consisted of an indiscriminate collection of the material underlying the forest, which forms a soil covering varying in depth with the density of the forest. It was composed chiefly of needles, leaves, bark, small twigs, and scattered cones, which were somewhat dry and brittle from exposure to the elements. The bark was collected from logs going into the mill, therefore was not kiln-dried as was the sawdust. All materials, after drying, were finely ground and stored in paper bags in a dry room. In a few experiments needles and leaves were used before they were completely dry. These will be designated in the data to follow.

Soils

Samples of Helmer silt loam the supposedly toxic timber soil were collected near the center of a cut-over area. The soil is a grayish or brownish yellow to pale yellow silt loam to a depth of 6 to 10 inches, underlaid to a depth of 24 to 30 inches by a non-calcareous pale yellow to yellowish-gray, powdery silt loam. This passes into a yellowish-gray to drab compact silt loam to silty clay loam, which usually extends to a depth of 36 to 50 inches. The surface soil contains a relatively small amount of decomposed organic matter and a relatively large amount of small roots, bits of wood, and other material from the forest. This material was largely screened out in the preparation of the sample for laboratory experiments. This particular field had been cleared for two years but was cropped only the year previous when it was seeded to oats. The yield was fair. The physical condition was unusually good con-

sidering the fact that the timber had been recently removed. Acidity as determined by the Truog method showed the soil to be medium acid.

Timber, garden, and field soils were chosen to determine the effects of the various forest materials on bacteriological activities.

This timber soil is unlike Helmer silt loam in origin and topography. It has a covering of loessal material underlaid with calcareous material of lake-bed origin at a depth varying from 10 inches to 2 feet. It represents a large acreage of soil in northern Idaho, and like the Helmer silt loam is a forest soil which produces very poorly. This type was collected from four different localities, each sample being used separately in experiments. The results obtained with this type of soil are the work of the previous bacteriologist in charge.[1] The soil was found to be medium acid by the Truog test.

The garden soil was a very rich one from the experiment station farm. It had been heavily manured two years previous, and some of the manure was still undecomposed in the soil. This manure was carefully avoided in the selection of the sample and that which was included was largely screened out in the later preparation of the sample. This soil was slightly acid by the Truog test.

The field soil was taken from a corn field at the experiment station farm in August 1920. This type represents a large acreage in northern Idaho—a fertile silt loam of light color and great depth—which never fails to produce well. It was found to be slightly acid by the Truog test.

All soil samples were carefully screened and stored in galvanized iron cans until used. The moisture content at the time of collection was approximately 15 per cent in all cases. This moisture content was maintained in the stored sample. They were stored in a building entirely separate from the laboratory and the temperature was approximately that found in the field.

METHODS

Ammonification

One-hundred-gram samples of the soil were weighed into wide-mouth bottles of 500 cc. capacity. One gram of dried blood was added to each, the contents thoroughly stirred, and the moisture brought to 25 per cent. An additional 2 gm. of water was added for each gram of blood and each gram of wood or other tree product under test. The bottles were plugged with cotton and incubated at 28°C. for 24 hours, then thoroughly stirred to insure equal distribution of moisture and other materials. They were then incubated for an additional 6 days, at the end of which period they were analyzed for ammonia content. This was determined by transferring the samples to copper flasks of 800-cc. capacity, adding approximately 5 gm. of heavy magnesium oxide and a small piece of paraffin to prevent foaming, and distilling the contents into

[1] T. L. Hills, former Assistant Bacteriologist, Idaho Agricultural Experiment Station.

standard sulfuric acid. The receiving flasks were transferred to a hot plate and boiled to approximately 100 cc. The excess acid was then titrated, using methyl red as indicator.

Nitrification

The samples for nitrification were prepared in the same manner as those for ammonification except that the moisture content was made 20 per cent. In some of the experiments ammonium sulfate, casein, and gelatin were used as the nitrifiable substance. In those cases the nitrogenous material was added from sterile standardized solution by volume at the same time the water was added to bring the moisture to 20 per cent. The samples were incubated at 28°C. for 4 weeks. Each week the moisture lost by evaporation was restored. At the end of the incubation period the samples were removed from the incubator, sufficient water added to bring the total water content to 400 cc., and the samples shaken at 15-minute intervals for 2 hours. Calcium oxide was then added as a flocculating agent, and the contents filtered through folded filters. Aliquots of the filtrate were evaporated to dryness in porcelain evaporating dishes and nitrate determined by the phenolsulfonic acid method.

In a few preliminary experiments sterile glass tumblers with petri dish covers were used as containers for the individual samples. The superiority of the wide-mouth bottle as a time and labor saver was soon recognized. The bottle plugged with cotton also affords better and more uniform aeration.

Denitrification

The samples for denitrification were prepared the same as those for ammonification. Definite amounts of standard sodium nitrate in solution were used instead of ammonium sulfate or dried blood.

RESULTS

Ammonification and nitrification, Helmer silt loam

Preliminary tests were made with the sample of Helmer silt loam to determine its ammonifying and nitrifying power. Thirty milligrams of nitrogen in the form of casein and blood was used to determine the ammonifying power, both with and without calcium carbonate. For determining the nitrifying power, 30 mgm. of nitrogen in the form of gelatin, casein, ammonium sulfate, and 1 per cent blood were used, each with and without calcium carbonate. The results of these tests are set forth in tables 1 and 2.

Table 1 shows that the supposedly toxic timber soil, Helmer silt loam, is not deficient in its power to convert organic nitrogenous material to ammonia. In the samples containing casein 95.4 per cent of the nitrogen was converted to ammonia. The efficiency of the soil to convert nitrogen in the form of casein or blood to ammonia is not increased by the addition of lime.

A study of the data in table 2 reveals the fact that the nitrifying power of this soil is very poor indeed. Whether it is the result of forest growth, or other cause, the fact remains that its power to convert organic nitrogenous material or ammonium sulfate to nitrate is practically nil. This condition in the soil is corrected by the application of calcium carbonate. The ability of the soil to form nitrate from casein, blood, and gelatin is not due to lack of ammonification of these substances, as is seen from the data in table 1. The acidity of the soil is no doubt a large factor in the low nitrate formation; samples of Helmer silt loam from many different localities with varying degrees of acidity have been used in these tests and results in accord with those presented above have been obtained.

TABLE 1

Ammonification in Helmer silt loam, timber soil

SAMPLE NUMBER	TREATMENT PER 100 GM. OF SOIL	NITROGEN AS AMMONIA
		mgm.
1– 4	None	1.40
5– 8	1 per cent $CaCO_3$	1.32
9–12	30 mgm. nitrogen (in casein)	28.60
13–16	30 mgm. nitrogen (in casein) and 1 per cent $CaCO_3$	27.70
17–20	1 per cent blood	35.35
21–24	1 per cent blood and 1 per cent $CaCO_3$	33.55

TABLE 2

Nitrification of various substances in Helmer silt loam, timber soil

SAMPLE NUMBER	TREATMENT PER 100 GM. OF SOIL	NITROGEN AS NITRATES	
		No $CaCO_3$	$CaCO_3$ 2 per cent
		mgm.	*mgm.*
1– 6	None	3.63	4.90
7–12	1 per cent blood	7.27	42.10
13–18	30 mgm. nitrogen (in gelatin)	7.11	23.88
19–24	30 mgm. nitrogen (in casein)	8.00	28.57
25–30	30 mgm. nitrogen (in ammonium sulfate)	4.77	36.36

Effect of sawdust on ammonia accumulation from blood in timber soil

The four samples of timber soil previously described were used to determine the effect of sawdust, with and without calcium carbonate, on ammonia accumulation from blood. Since the results secured with each sample were similar, only the average of the four samples is given in figure 1. The sawdust was applied at the rate of 1.5 gm. to 100 gm. of soil to which the blood and calcium carbonate were applied at the rate of 1 gm. per 100 gm. of soil.

It is seen from the data in figure 1 that sawdusts from the various woods reduced ammonia accumulation. Cedar was decidedly most toxic, while maple was next, with the other woods following with more or less toxicity.

Cedar reduced ammonia accumulation 78.9 per cent, while white pine, the least detrimental of the group, reduced it 13.1 per cent. Calcium carbonate tends to decrease the toxicity, but in no case is the ammonia accumulation equivalent to that in the control without the calcium carbonate. Ammonification in this soil is very good, better, in fact, than in the productive field soil used in later experiments.

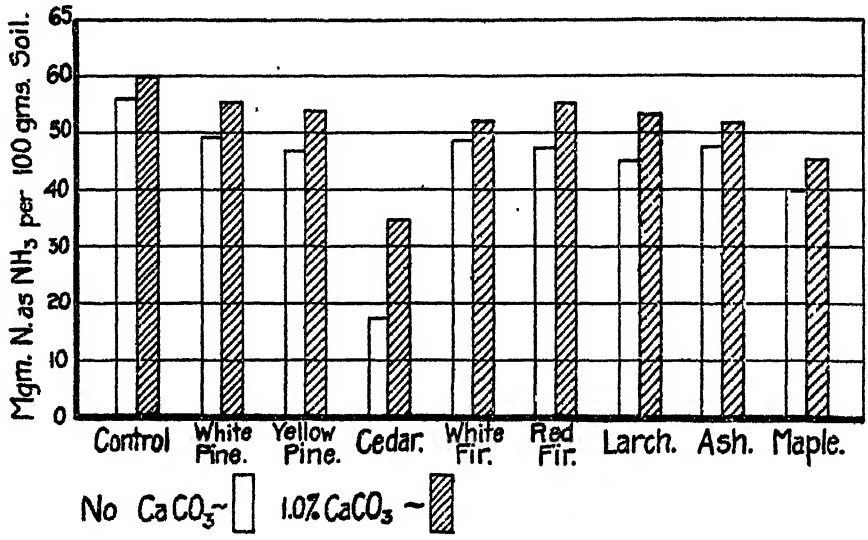


FIG. 1. EFFECT OF SAWDUST ON AMMONIA ACCUMULATION FROM BLOOD IN TIMBER SOIL

Effect of woods and tree products on ammonia accumulation from blood in field soil

The foregoing ammonification experiments to test the effect of woods were repeated, using the productive field soil previously described. The quantities of the various tree products used were 1.0 and 1.5 per cent of the weight of the soil sample; the quantity of blood used was 1.0 per cent. Results are given in figure 2 which show that all treatments reduced ammonia accumulation except the 1 per cent applications of white pine, yellow pine, and white fir sawdusts and larch needles. Of the sawdusts, cedar exerted the greatest retarding influence followed by red fir, maple, and larch. This agrees closely with the results obtained with the timber soil, in which case cedar was followed by maple and larch, with the others grouped near fourth place. Among the tree products other than sawdust, cedar needles were the most detrimental, followed by yellow pine, white pine, and white fir needles. Larch needles, and white and yellow pine sawdusts, show but little retarding influence.

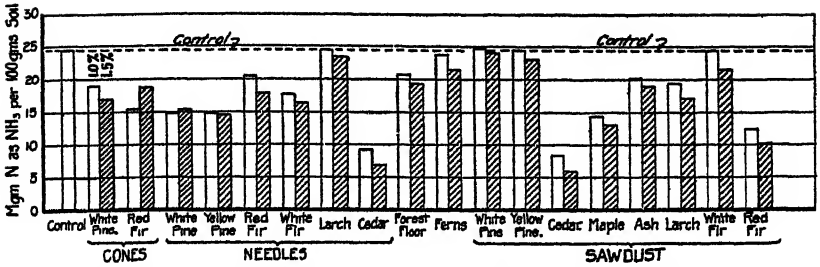


FIG. 2. EFFECT OF TREE PRODUCTS ON AMMONIA ACCUMULATION FROM BLOOD IN FIELD SOIL

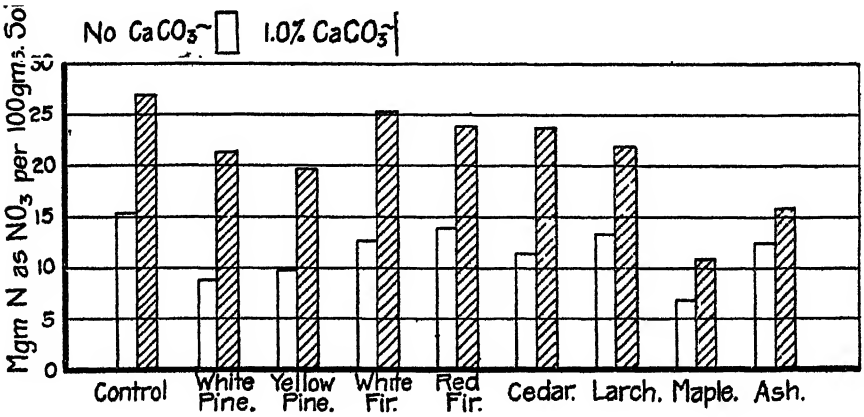


FIG. 3. EFFECT OF SAWDUST ON NITRIFICATION OF AMMONIUM SULFATE IN TIMBER SOIL

Effect of sawdust on the nitrification of ammonium sulfate in timber soil

One-hundred-gram samples of timber soil were treated with 1.5 per cent sawdust from the various woods and 30 mgm. nitrogen in the form of ammonium sulfate, both with and without 1.0 per cent calcium carbonate. Four samples of soil were used. The average results are given in figure 3 which show that all treatments inhibited nitrate formation from ammonium sulfate. In the absence of calcium carbonate maple caused the greatest retardation, with white pine, yellow pine, and cedar following in order. This is not the order of toxicity found in the ammonification experiments, white pine having the least influence in that case. In the presence of calcium carbonate the order of toxicity is somewhat changed, maple having the greatest retarding influence, followed by ash, yellow pine, and white pine. There is a marked response to the application of calcium carbonate. The detrimental action of the various woods is in no sense overcome, however, since the response in the control is equally as great as in the others. This is probably due to the fact that the calcium carbonate corrects natural conditions in the soil unfavorable to the nitrifying organisms.

Effect of sawdust on the nitrification of ammonium sulfate in field soil

The nitrification experiments described above were repeated with the productive field soil to determine if the productiveness of the soil was a factor in the detrimental action of the woods. Sawdust was applied in amounts of 1.0 to 3.0 per cent by weight, and 30 mgm. of nitrogen in ammonium sulfate was added to each 100 gm. of soil. The results given in figure 4 show that ash sawdust had the greatest retarding influence followed very closely by maple, then cedar, white and yellow pine. Three per cent of ash and maple sawdust stopped practically all nitrate formation, and 1 per cent reduced it by nearly one-half. The results secured with this soil are similar to those obtained with the timber soil.

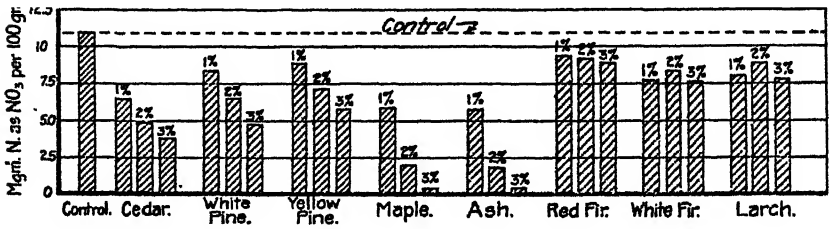


FIG. 4. EFFECT OF SAWDUST ON THE NITRIFICATION OF AMMONIUM SULFATE IN FIELD SOIL

Effect of sawdust on the nitrification of blood in field soil

Sawdust was applied to the field soil and garden soil previously described at rates of 1 to 2.5 gm. per 100 gm. of soil. All samples received 1 per cent of dried blood. The results obtained with the field soil are set forth in table 3 and are represented diagrammatically in figure 5, while those with the garden soil appear in table 4 and figure 6.

It will appear from a study of tables 3 and 4 that there is a discrepancy between amounts of wood 1.5 and 2.0 per cent, and that the 2.0 per cent has nitrified to a further degree than the 1.5 per cent. A more careful study will show this is not the case. The number of samples of soil to handle in connection with the work was so great it became necessary to run concentrations 1.0 and 1.5 per cent at one time, and 2.0 and 2.5 per cent at a later date. The controls run at different times did not always form the same amount of nitrate, although conditions were controlled as well as could be. It will be noted in table 3 that the control for 1 and 1.5 per cent sawdust was 31.7 mgm. nitrogen, while the control for 2 and 2.5 per cent,which was run at a later date, was 36.3 mgm. nitrogen. The double line between concentrations 1.0 and 1.5 per cent on the one side, and 2.0 and 2.5 per cent on the other, indicates that they were run at different times. The data in these tables are converted to percentage

efficiency, considering the control in each case as 100 per cent, and are set forth in charts 5 and 6. This change makes comparable the data accumulated at various times.

It is seen from the data in tables 3 and 4, and figures 5 and 6 that all the sawdusts tended to reduce nitrification of blood. In general this action in-

TABLE 3

Effect of sawdust on the nitrification of blood in field soil

SOURCE OF SAWDUST	NITROGEN AS NITRATE PER 100 GM. OF SOIL			
	1 per cent*	1.5 per cent*	2 per cent*	2.5 per cent*
	mgm.	*mgm.*	*mgm.*	*mgm.*
Control	31.7	31.7	36.3	36.3
White pine	29.1	28.0	31.9	30.9
Yellow pine	29.6	28.0	29.1	29.1
Cedar	16.3	12.3	10.4	8.4
Maple	26.9	23.7	24.5	21.0
Ash	27.6	30.1	31.7	30.5
Larch	27.8	26.9	32.7	30.5
White fir	29.2	31.2	35.5	35.1
Red fir	31.0	30.0	31.1	29.8

* The percentages refer to the amount of sawdust mixed with the soil and are based on the weight of the soil sample.

TABLE 4

Effect of sawdust on the nitrification of blood in garden soil

SOURCE OF SAWDUST	NITROGEN AS NITRATE PER 100 GM. OF SOIL			
	1 per cent*	1.5 per cent*	2 per cent*	2.5 per cent*
	mgm.	*mgm.*	*mgm.*	*mgm.*
Control	66.6	66.6	49.2	49.2
White pine	58.3	60.8	41.0	39.8
Yellow pine	63.6	63.6	39.0	40.3
Cedar	63.6	58.3	17.3	10.7
Maple	63.6	56.0	29.4	31.1
Ash	63.6	63.6	38.6	38.0
Larch	60.8	63.6	38.6	34.4
White fir	63.6	60.8	33.0	47.1
Red fir	63.6	63.6	41.1	45.0

* The percentages refer to the amount of sawdust mixed with the soil and are based on the weight of the soil sample.

creases with increasing amounts of sawdust, but not always. The experiments were repeated many times and irregularities were always noted. Cedar was the most toxic, followed by maple, larch, ash, and the pines. The order of toxicity was the same for both soils, even though the garden soil contained a large amount of organic matter and should have been better able to overcome the toxic material.

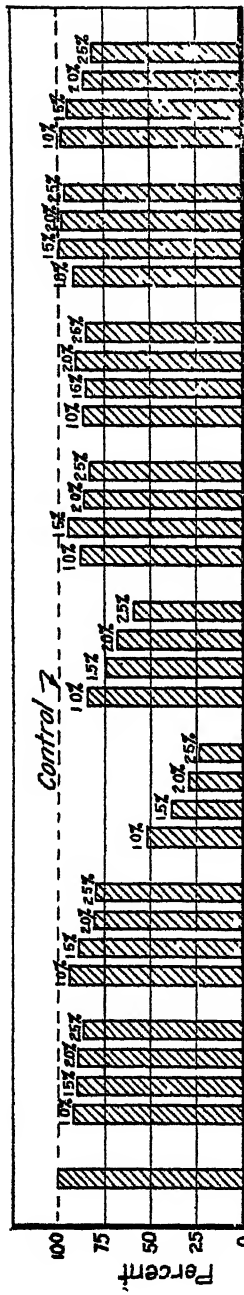


FIG. 5. EFFECT OF SAWDUST ON THE NITRIFICATION OF BLOOD IN FIELD SOIL

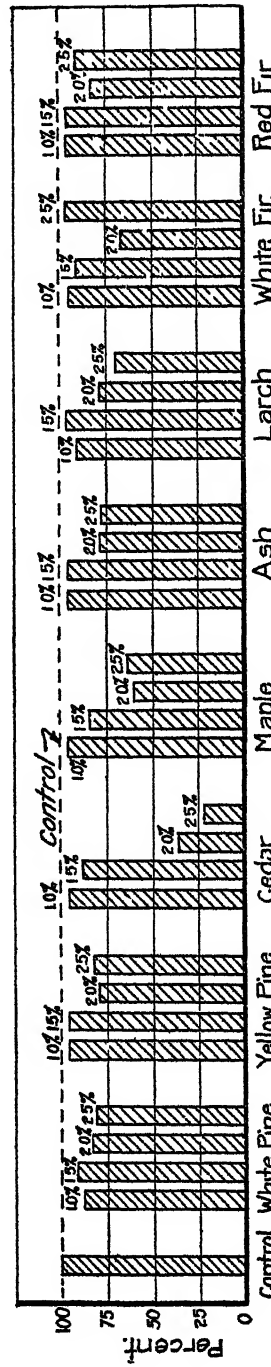


FIG. 6. EFFECT OF SAWDUST ON THE NITRIFICATION OF BLOOD IN GARDEN SOIL

It will be noted that the order of toxicity of the sawdusts is very similar in charts 4 and 5.

Effect of sawdust on the nitrification of blood in the presence of calcium carbonate in field and garden soils

The experiments to determine the effect of sawdust on the nitrification of blood with both field and garden soil were repeated with the addition of 1 gm. of calcium carbonate for each 100 gm. of soil. The results are given in table 5.

TABLE 5

Effect of sawdust on the nitrification of blood in the presence of 1.0 per cent calcium carbonate in field and garden soils

SOURCE OF SAWDUST	NITROGEN AS NITRATE PER 100 GM. OF SOIL			
	Field soil		Garden soil	
	1 per cent*	1.5 per cent*	1 per cent*	1.5 per cent*
	mgm.	*mgm.*	*mgm.*	*mgm.*
Control	75.8	75.8	123.9	123.9
White pine	72.7	70.3	123.9	118.6
Yellow pine	67.2	69.4	118.6	120.6
Cedar	64.0	56.9	120.6	107.7
Maple	58.7	52.8	107.7	96.5
Ash	64.3	61.4	118.6	112.0
Larch	70.8	64.3	116.6	113.8
White fir	68.1	67.2	86.8	86.8
Red fir	68.5	70.3	105.5	116.6

* The percentages refer to the amount of sawdust added to the soil and are based on the weight of the soil sample.

A great response to the application of calcium carbonate is noted in both soils. The toxic action of the various sawdusts is in no case overcome by the calcium carbonate but it was not nearly so marked as in its absence. The amount of nitrate formed was larger in the presence of each sawdust with lime than in the control without lime and sawdust. The order of toxicity was not the same with each soil. Maple, cedar, ash and white fir were, however, the most detrimental in each soil.

Effect of tree products on the nitrification of ammonium sulfate in field soil

One-hundred-gram samples of the field soil were treated with 30 mgm. of nitrogen in ammonium sulfate and the various forest products in amounts ranging from 1 to 3 per cent to determine the effect on nitrate formation. The results are given in figure 7.

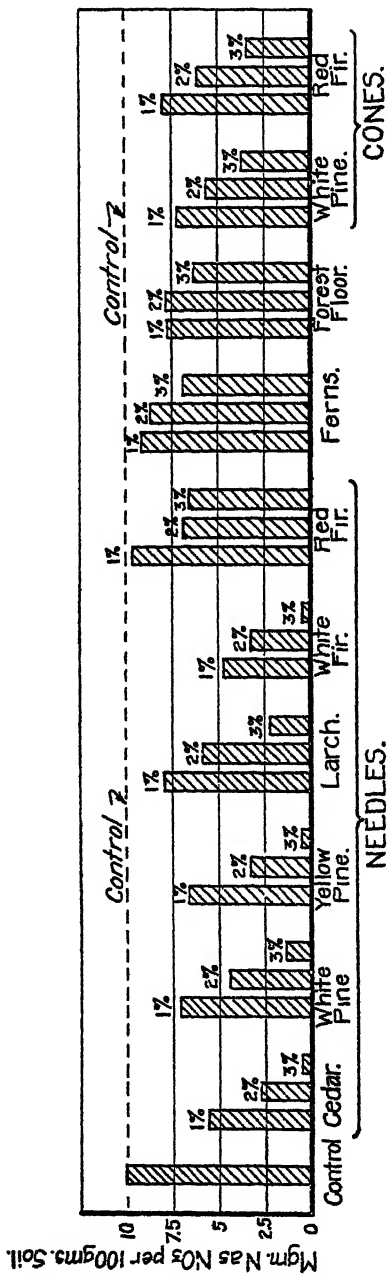
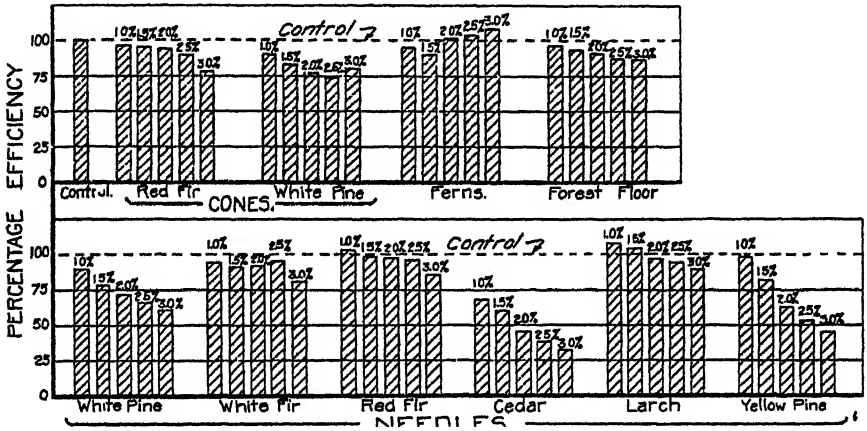


FIG. 7. EFFECT OF TREE PRODUCTS ON THE NITRIFICATION OF AMMONIUM SULFATE IN FIELD SOIL

The data in figure 7 show an inhibiting action by all the substances tested. White fir needles proved the most toxic, followed by cedar needles, and yellow and white pine needles. Ferns proved the least detrimental. It is interesting to note that white fir sawdust was the least toxic of the sawdusts towards nitrate formation, while the needles proved the most toxic. The addition of 3 per cent white fir, yellow pine, and cedar needles practically eliminated nitrate formation from ammonium sulfate.

Effect of tree products on the nitrification of blood in field and garden soils

The various forest products were applied to the soil in amounts ranging from 1 to 3 per cent to determine their effect on nitrification of blood. The


PERCENTAGE EFFICIENCY
Control
Control
Control

results are given in figures 8 and 9, expressed in percentage efficiency considering the control as 100 per cent efficient.

It is seen from the data in figures 8 and 9 that the various products do not exert as marked a toxic action toward nitrification of blood as of ammonium sulfate, and also that the order of toxicity is not the same in the two soils. In the field soil cedar needles are quite toxic, followed by yellow and white pine needles. Red fir cones, ferns, larch needles, and red fir needles show little toxicity. In the garden soil the order of toxicity is yellow pine, white fir, red fir, white pine, and cedar needles. Red fir cones and ferns are very slightly toxic. Here again the white fir needles proved among the most toxic while the sawdust exerts but little toxicity in the same soil.

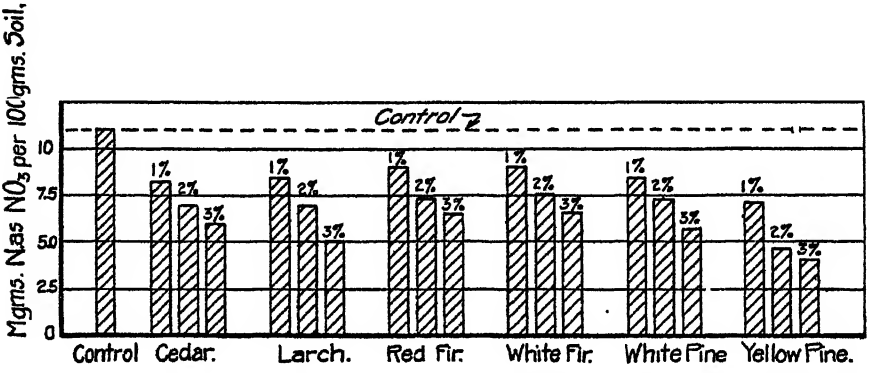


FIG. 10. EFFECT OF BARK ON THE NITRIFICATION OF AMMONIUM SULFATE IN FIELD SOIL

Effect of bark on the nitrification of ammonium sulfate in field soil

The finely ground bark, previously described, was applied to the soil in amounts ranging from 1 to 3 per cent to determine the action on nitrate formation from ammonium sulfate. The results are presented in chart 10.

It will be seen from the data in figure 10 that all the barks exerted a toxic action toward nitrate formation. Yellow pine was the most toxic of the barks tested, with the other species grouped very closely.

Effect of woods on denitrification in field soil

Tests were made to determine if the various sawdusts would act as energy for the denitrifying organisms and thus cause loss of nitrate nitrogen through reduction. If this were the case the results obtained in the nitrification experiments would not be due to a toxicity to those organisms but to a stimulation of the denitrifying group.

One-hundred-gram samples of the field soil were weighed into wide-mouth bottles of the same type used in the other experiments. One series received amounts of nitrogen as nitrate in amounts ranging from 10 to 120 mgm. per 100 gm. of soil. In a second series all samples received 30 mgm. nitrogen as nitrate

and 1.5 gm. of sawdust but a different kind of sawdust was used in each case. In the third series 1.5 gm. of cedar sawdust was applied to each sample, and the nitrogen varied from 10 to 120 mgm. The fourth series was the same as the third except yellow pine was used in the place of cedar. All samples were run in quadruplicate. The results are given in table 6.

TABLE 6

Effect of woods on denitrification in field soil

NITROGEN AS NITRATE PER 100 GM. OF SOIL	SAWDUST (1.5 PER CENT)	NITROGEN AS NITRATE RECOVERED FROM 100 GM. OF SOIL	LOSS OR GAIN IN NITRATE
mgm.		*mgm.*	*mgm.*
10	None	16.26	6.26
20		23.53	3.53
30		33.33	3.33
60		64.51	4.51
120		111.11	−8.89
30	None	33.70	3.70
30	Cedar	33 33	3.33
30	Maple	20.70	−9.30
30	Ash	26.50	−3.50
30	Larch	29.40	−0.60
30	White pine	29.70	−0.30
30	Yellow pine	28.20	−1.80
30	Red fir	32.26	2.26
30	White fir	31.22	1.22
10	Cedar	14.09	4.09
20		25.64	5.64
30		34.48	4.48
60		60.60	0.60
120		109.17	−10.83
10	Yellow pine	10.72	0.72
20		18.18	−1.82
30		32.26	2.26
60		62.50	2.50
120		111.11	−8.89

It will be seen from the data in table 6 that maple, and possibly ash, are the only sawdusts which caused loss of nitrate. This experiment indicates that the toxicity obtained in the ammonification and nitrification experiments is not due to the action of denitrifying organisms, with the exception of maple, and possibly ash, but to a toxicity, or inhibition of the specific groups.

SUMMARY

Sawdusts from cedar, maple, ash, red fir, white fir, larch, and white and yellow pine, were collected from kiln-dried boards, carefully screened and used in amounts varying from 1 to 3 per cent to determine the effect on ammonia

accumulation from dried blood, nitrification of ammonium sulfate and dried blood and nitrate reduction in forest soils. Other tree products, such as leaves, needles, and cones from the above named trees, "forest floor," and ferns were similarly tested. Three types of soil were used in the tests, namely, a timber soil of low fertility, a field soil of average fertility, and a garden soil of high fertility.

All the substances under test reduced ammonia accumulation. In the timber soil cedar caused the greatest reduction, followed by maple. Cedar reduced ammonia accumulation 78.9 per cent when applied at the rate of 1.5 per cent by weight, while white pine, the least toxic of the group, reduced it but 13.1 per cent. The results with the field soil were very similar to those obtained with the timber soil. Cedar, maple, and larch were the most toxic. Among the products other than sawdust cedar needles exerted the greatest inhibitory action, followed by yellow pine, white pine, and white fir needles. Larch needles reduced ammonia accumulation only slightly.

All the substances tested proved inhibitory to nitrate formation from blood and ammonium sulfate. This action is not overcome by application of calcium carbonate. Ash and maple sawdust in 3 per cent applications practically stopped nitrification of ammonium sulfate in the field soil. Cedar, maple, larch, ash, and red fir sawdusts caused the greatest reductions in nitrification of blood and ammonium sulfate. Among the products other than sawdust, 3 per cent white fir, yellow pine, and cedar needles practically eliminated nitrate formation from ammonium sulfate. White fir sawdust was but slightly detrimental, while the needles were extremely so. Bark from the trees tested reduced nitrate formation from ammonium sulfate. The "forest floor," which consisted of the indiscriminate collection of the material underlying the forest and covering the soil, reduced nitrate formation from ammonium sulfate and blood. Ferns, which are abundant on cut-over lands, proved to have but slight effect and would seem, therefore, to have no economic importance.

The results of the denitrification experiments indicate that none of the substances tested, with the exception of maple and possibly ash, serve as energy for the denitrifying organisms.

The results of the entire work indicate that the low fertility, and apparent toxic condition of the Helmer silt loam, is in a large part due to the timber residue. This material collects continuously throughout the growing period of the forest, and due to its slow rate of decomposition has a direct effect upon the beneficial biological processes in the soil. The quantities of tree products used in the treatments were, in all probability, below those actually occurring in the forest soil under timber. The accumulation of the forest materials from year to year leads to a concentration which is detrimental to ammonification and nitrification. Maple and ash are not common in the Idaho forests, but the other forest materials which showed marked toxic action are abundant. This is particularly true of cedar and the pines. It is com-

monly thought that a period of three to five years is required for this timber residue to completely decompose and its detrimental action to disappear. The use of sawdust bedding is to be discouraged in case the sawdust is to be spread with the manure on the field.

CONCLUSIONS.

The various tree products tested proved inhibitory to ammonia and nitrate accumulation in three different types of soil.

Calcium carbonate does not overcome the inhibiting action of the various materials tested, but causes a general increase in nitrate formation.

Cedar sawdust was the most inhibitory of the sawdusts to ammonia accumulation from blood. The reduction in the timber soil was 78.9 per cent, while white pine, the least inhibitory of the sawdusts, caused a reduction of 13.1 per cent.

Cedar, maple, larch, ash, and red fir sawdusts had the greatest inhibiting action upon nitrate formation from ammonium sulfate and blood.

Among the materials other than sawdust, white fir, yellow pine, and cedar needles caused the greatest reductions in the nitrification of ammonium sulfate.

The indiscriminate collection of material covering the soil under the forest, designated as "forest floor," reduced ammonia and nitrate accumulation in soil.

Ferns, common on cut-over soils, proved but slightly inhibitory and therefore of no economic importance.

Denitrification experiments indicated that the reduction of nitrate formation is not due to the denitrifying group, but to actual inhibition of the nitrifying organisms. Maple, and possibly ash, are exceptions, but are not common in the Idaho forests.

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THE CLARK HYDROGEN-ELECTRODE VESSEL AND SOIL MEASUREMENTS

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In certain soil studies specific chemical reaction must be accurately determined, and it is most accurately determined by measurement of the hydrogen-ion concentration.

Two methods are available for the measurement of hydrogen-ion concentration in soils—the colorimetric and the electrometric. The colorimetric method requires the use of soil extracts and color indicators of chemical reaction. Such indicators ionize, with production or change of color, in solutions containing definite hydrogen-ion concentrations. Wherry (1) has used a series of such indicators to determine the hydrogen-ion concentrations of soil extracts at various points between superacid and superalkaline soils. While such a method is more accurate than the older titration methods, yet it indicates the specific reaction of the soil indirectly.

The hydrogen ion carries a positive electric charge, thus maintaining an electric potential in the soil solution. The electrometric method measures this potential by means of a potentiometer and galvanometer; the electric potential in the soil solution being balanced against a known resistance, the accuracy of such measurements depending upon the stability of this balance. Gillespie and Hurst (2) have devised a hydrogen-electrode vessel for soil measurements which very nearly yields a steady potential balance. Using the Clark hydrogen-electrode vessel we obtained a steady potential balance and satisfactory electrometric measurements of specific soil reactions.

In field studies and in studies of processes constant over a wide range of hydrogen-ion concentrations, an approximate determination is sufficient, and the colorimetric method may be used. In more particular studies and when processes may be seriously affected by the hydrogen-ion concentration of the solution, the electrometric method should be used because it is the most accurate method available.

The apparatus used in this investigation consisted of the Clark hydrogen-ion apparatus supplied by the Leeds and Northrup Company, a portable lamp and scale galvanometer, a Leeds and Northrup type K potentiometer and a standard Weston cell, Model 4. Two Columbia dry cells furnished the working current. Hydrogen obtained from a Kipps' generator was passed through two wash bottles (the first containing 0.5 *N* NaOH and a small quantity of lead

acetate; the second containing distilled water) and then conducted into the hydrogen-electrode vessel. A normal KCl calomel electrode was used and normal KCl solution, saturated with calomel, was used in the connecting vessel. Measurements were made at room temperature without the aid of a constant temperature bath, but the temperature of the calomel electrode was carefully noted immediately following each measurement, the reading being made to the nearest degree or half-degree Centigrade. Following Clark's suggestions, hydrogen was not bubbled through the sample under measurement. Clark (3) states that "in fluids containing carbonate the double effect of the CO_2 upon the partial pressure of hydrogen and upon the hydrogen-ion equilibrium renders accurate measurements difficult. It is of more importance to maintain the original CO_2 content of the solution than it is to be concerned about the effect of CO_2 upon the partial pressure of hydrogen." The platinum electrodes were coated with platinum black at intervals of four to seven weeks and kept in distilled water during the intervals; they were saturated with hydrogen immediately before each day's series of measurements.

To test the accuracy of the electrometric measurements made by such an apparatus under the above conditions, a 0.1 *N* HCl solution was measured with the results shown in table 1.

TABLE 1

	TIME	READING	TEMPERATURE	pH VALUE	THEORY
		volts	°C.		
0.1 *N* HCl, factor 1.0006	10.20	0.3490	31	1.06	1.07 (4)
	10.22	0.3490			
Duplicate	10.37	0.3475	31	1.08	
	10.39	0.3475			

As a further test two standard "buffer" solutions were measured electrometrically and colorimetrically. Results are given in table 2.

The colorimetric method measures to two-tenths of a pH value. Tables 1 and 2 demonstrate that without extensive equipment electrometric measurements of hydrogen-ion concentrations afford a fair degree of accuracy. Great refinement in correcting for barometric and temperature fluctuations is necessary only in physio-chemical research.

In making the soil measurements the hydrogen-electrode vessel was half filled with CO_2-free distilled water, a small portion of water entering the reservoir; 4 gm. of air-dried, or 5 gm. of fresh soil were introduced in small portions into the vessel, carefully mixing the soil and water; the vessel was completely filled with CO_2-free distilled water, the platinum electrode carefully inserted, avoiding the formation of air bubbles; the stopcocks closed, and the vessel placed in an inverted position in the shaking apparatus and connected with the hydrogen generator in the usual manner. In this inverted position

the soil settles upon the upper surface of the vessel making it possible to sweep out the water with hydrogen. As much water as possible was swept out with

TABLE 2

	TIME	READING	TEMPERATURE	ELECTROMETRIC pH VALUE	COLORIMETRIC pH VALUE
		volts	°C.		
Buffer solution 1	2.17	0.6995	32	6.88	7.0
	2.19	0.6995			
Duplicate	2.43	0.6995	32	6.88	7.0
	2.45	0.6995			
Buffer solution 2	3.06	0.7670	32	7.99	8.2
	3.08	0.7670			
Duplicate	3.26	0.7675	32	8.00	8.2
	3.28	0.7675			

TABLE 3

	ELECTRODE VESSEL	TIME	READING	TEMPERATURE	pH VALUE
			volts	°C.	
Silt loam, 20	1	10.56	0.7235	21.0	7.50
		10.58	0.7235		
	1	11.10	0.7420	25.0	7.55
		11.12	0.7420		
	1	11.46	0.7290	20.5	7.61
		11.48	0.7290		
Average					7.55
Silt loam, 20	2	12.21	0.7270	25.0	7.48
		12.23	0.7270		
	2	12.33	0.7340	20.5	7.69
		12.35	0.7340		
	2	3.41	0.7385	20.5	7.77
		3.43	0.7385		
	2	4.25	0.7240	20.5	7.53
		4.27	0.7240		
Average					7.62

hydrogen, the stopcocks closed, the vessel disconnected and removed from the shaking apparatus. The vessel was now shaken by hand for 5 minutes, then

placed in the proper position in the shaking apparatus and so adjusted that the platinum electrode was completely submerged in the wet soil. After three minutes the vessel was so re-adjusted that the platinum electrode was half immersed in the wet soil, and the connections were made with the potentiometer, the apparatus remaining undisturbed for six minutes, after which the readings were made.

To test the accuracy of such electrometric measurements different hydrogen-electrode vessels and different platinum electrodes were used to measure the same soil. Results are shown in table 3.

Having established a fair degree of accuracy for the electrometric measurements, six samples of fresh soils from the Station farm were measured as in table 4.

TABLE 4

Fresh soils

	READING	TEMPERATURE	pH VALUE	AVERAGE
	volts	°C.		*pH*
Silt loam, 1. 26.6 per cent H_2O	0.6000	19.0	5.41	5.31
Duplicate	0.5890	19.0	5.22	
Silt loam, 2. 26.6 per cent H_2O	0.6020	19.0	5.45	5.46
Duplicate	0.6050	20.0	5.48	
Silt loam, 3. 25 per cent H_2O	0.5940	19.5	5.30	5.43
Duplicate	0.6100	20.0	5.57	
Silt loam, 4. 25 per cent H_2O	0.5880	20.0	5.19	5.37
Duplicate	0.6090	20.0	5.55	
Silt loam, 5. 25 per cent H_2O	0.6100	22.0	5.54	5.69
Duplicate	0.6280	22.0	5.85	
Silt loam, 6. 25 per cent H_2O	0.6180	21.5	5.51	5.66
Duplicate	0.6250	21.5	5.81	

The same samples of soil were air-dried, passed through a 1 mm. sieve, stored in Mason jars on the laboratory table for 12 weeks and then remeasured as in table 5.

These air-dried soils, together with a strongly acid soil (silt loam, 17), were measured colorimetrically using Wherry's method. The results are tabulated together with their electrometric measurements in table 6.

Hopkins test showed a lime requirement of 108 pounds of calcium carbonate for soils 1, 2 and 4; 140 pounds for soil 3; 36 pounds for soils 5 and 6; and 1786 pounds for soil 17. Soils 1 to 6 are similar in character and highly phosphatic; soil 17 is of a different type and moderately phosphatic.

TABLE 5

Soils after air-drying

	READING	TEMPERATURE	pH VALUE	AVERAGE pH VALUE	
				Air-dried	When fresh
	volts	*°C.*			
Silt loam, 1	0.5970	31.5	5.19	5.23	5.31
Duplicate	0.6030	32.0	5.28		
Silt loam, 2	0.6030	31.5	5.29	5.09	5.46
Duplicate	0.5790	31.5	4.89		
Silt loam, 3	0.5840	30.5	4.98	4.98	5.43
Duplicate	0.5840	31.0	4.98		
Silt loam, 4	0.5730	31.0	4.80	5.02	5.37
Duplicate	0.6010	31.5	5.25		
Silt loam, 5	0.6190	32.0	5.54	5.52	5.69
Duplicate	0.6165	31.5	5.51		
Silt loam, 6	0.6000	30.0	5.26	5.37	5.66
Duplicate	0.6140	30.0	5.49		

TABLE 6

SOIL	SPECIFIC REACTION	pH VALUE	
		Colorimetric	Electrometric
	acid		
1	3+	6.6	5.23
2	3+	6.6	5.09
3	3+	6.6	4.98
4	3+	6.8	5.02
5	3+	6.5	5.52
6	3+	6.6	5.37
17	10	6.0	3.44

SUMMARY

The hydrogen-ion concentration of the fresh and of the air-dried soils studied may be measured directly by using the Clark hydrogen-electrode vessel.

The air-dried soils measured in this manner show a slightly greater hydrogen-ion concentration than they do when measured in a fresh condition, and a distinctly greater hydrogen-ion concentration than they do when measured by Wherry's method.

It has been shown that without extensive equipment electrometric measurements of hydrogen-ion concentrations in these soils afford a fair degree of accuracy.

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MICROÖRGANISMS CONCERNED IN THE OXIDATION OF SULFUR IN THE SOIL: III. MEDIA USED FOR THE ISOLATION OF SULFUR BACTERIA FROM THE SOIL[1]

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It has been known for a long time that sulfur and its compounds can be oxidized by various groups of bacteria, and in this process the sulfur is used, in place of carbon compounds, as a source of energy. The carbon necessary for the building up of the protoplasm of the organisms is obtained either from carbonates or from the CO_2 of the atmosphere. The various microörganisms concerned in the oxidation of sulfur and sulfur compounds are all brought together into one large group, under the name of sulfur bacteria. However, the fact that these organisms vary greatly both in their morphology and metabolism has led various investigators to subdivide them into several groups. The earlier investigations of Winogradsky (17) and other investigators on Beggiatoa, Thiothrix, purple bacteria, etc., used, primarily, hydrogen sulfide and sulfides as a source of sulfur. These substances are presumably oxidized first to sulfur and then to sulfuric acid. The organisms were grouped together by Omelianski under "sulfur" bacteria. They are usually subdivided as by Omelianski (12) and Düggeli (2) as follows:

1. Thread forming, colorless bacteria, accumulating sulfur within their cells.
2. Non-thread forming, colorless bacteria, accumulating sulfur within their cells.
3. Purple bacteria.

As a result of the work of Nathanson in 1902 (11), Beijerinck (1) and Jacobsen (5, 6), on the oxidation of thiosulfate, a new group of organisms was described. These bacteria are colorless, non-thread forming, and use thiosulfate as a source of energy; they do not accumulate any sulfur within their cells but produce an abundance of sulfur outside of their cells. These bacteria were naturally placed in a fourth and new group under the name of "thiosulfate" bacteria, or, according to Omelianski (12), "thionic acid" bacteria.

Recently a fifth group of sulfur bacteria has been added. This includes the organism which is concerned in the oxidation of elementary sulfur in the so-called "sulfur-floats-soil" composts, developed by Lipman (8), McLean (10) and their associates. This organism isolated by the author and associates

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(9, 14, 15, 16) is able to oxidize elementary sulfur very rapidly to sulfuric acid. It is a small, colorless, non-thread forming organism, using primarily elementary sulfur as a source of energy, not accumulating any sulfur within or without its cells. This organism (*Thiobacillus thiooxidans*) can be readily isolated in pure culture, by the use of proper media, and can be kept in culture more readily than most of the sulfur organisms studied so far.

The classification of the organisms concerned in the oxidation of sulfur into I, sulfur bacteria, including the first 3 groups, and II, thionic acid bacteria, including group 4, might be modified in view of the discovery of *Thiobacillus thiooxidans*. This modification would consist in dividing the sulfur bacteria, if physiological characteristics are taken as a basis of subdivision, into 3 large groups: I. "Sulfide" bacteria, which would take the place of Omelianski's "sulfur" bacteria. Into this group we would include organisms which oxidize primarily H_2S and sulfides, with the accumulation of sulfur within the cells of the organisms. The first three smaller groups (arabic numerals) would be included into this large group (I). II. "Thiosulfate" or "thionic acid" bacteria, which oxidize primarily thiosulfates, to some extent sulfides and elementary sulfur with the accumulation of sulfur outside of their cells and the transformation of sulfur compounds into sulfates and persulfates. This group would include the small group, no. 4, which is the same as Omelianski's second group. III. "Sulfur" bacteria proper, organisms which oxidize primarily elementary sulfur, without accumulating any sulfur within or without the cells, but with the production of large amounts of acid formed by the oxidation of sulfur. This large group would include organisms like those studied by the author and associates (group 5).

From the systematic point of view, the members of group I (1, 2, 3) belong partly to the *Thiobacteriales*, partly to other groups, while groups II and III (4, 5) belong to one genus *Thiobacillus* closely related to the other autotrophic bacteria among the *Eubacteriales*.

However, this new system would not present greater advantages over the old in view of the fact that organisms belonging to group II can also oxidize elementary sulfur, and organisms in group III can also use, to a small extent, sulfides and thiosulfates.

The subdivision of the organisms concerned in the oxidation of sulfur and its compounds directly into the minor five groups gives a good working basis. Of these five groups only 4 and 5 are found in the soil or may become active there in oxidizing sulfur; the studies presented in this as well as in the following papers will be limited to these 2 groups. Group 1 (Beggiatoa, etc.) has so far not been demonstrated in normal, cultivated soils. This is also true of the purple bacteria,—it is not even definitely established, as far as pure cultures are concerned, that these organisms are able to oxidize sulfur compounds. Representatives of group 2 have been mentioned as soil organisms by Gicklehorn (4), but the work of this investigator consisting merely in examining microsopically impure cultures, without any attempt to a study of pure cultures and

physiological activities, deserves little consideration. Groups 4 and 5, the first studied by Nathanson (11), Beijerinck (17), Jacobsen (5, 6), Lieske (7), Gehring (3), and Trautwein (13), the second by the author and associates (9, 14, 15, 16), deserve careful consideration as soil microörganisms.

So far, three species belonging to these 2 groups have been described: *Thiobacillus thioparus* Beijerinck, *Thiobacillus denitrificans* Beijerinck, and *Thiobacillus thiooxidans* Waksman and Joffe. All these three organisms are autotrophic deriving their carbon from CO_2; however, the form related to *Th. denitrificans* isolated by Trautwein can also thrive on organic carbon compounds. *Th. thioparus* and *Th. denitrificans* were placed in group 4 and *Th. thiooxidans* in group 5. The differentiating characters between these two groups can be summarized under the following headings:

A. The organisms placed in group 4 were isolated by the use of thiosulfate as a source of sulfur, although they are also able to oxidize H_2S, sulfides and even elementary sulfur. *Thiobacillus thiooxidans* was isolated by the use of elementary sulfur (powdered); it oxidizes thiosulfate and sulfides only to a small extent.

B. The *Th. thioparus* and *Th. denitrificans* produce free sulfur outside of their cells in the form of a pellicle. Trautwein (13) recently described an organism related to *Th. denitrificans*, but which grows aerobically and does not accumulate any sulfur. *T. thiooxidans* does not produce any sulfur from thiosulfate, which is rapidly oxidized to sulfuric acid.

C. *Th. thioparus* and *Th. denitrificans* are according to Beijerinck (1) $3 \times 0.5 - 1\mu$ in size, motile, and can be cultivated on agar media. The denitrifying sulfur oxidizing organisms studied by Lieske and Gehring are only 1μ long. The organism studied by Trautwein is $1\text{–}2 \times 0.5\mu$, motile and reduces nitrates, under anaerobic conditions. *Th. thiooxidans* is 0.75–$1 \times 0.5\mu$, non-motile, was not cultivated so far on solid media.

D. The organisms belonging to group 4 oxidize the thiosulfate to sulfate and persulfate, according to Nathanson (11) and Trautwein (13), while the *Th. thiooxidans* oxidizes thiosulfate to sulfate, which will explain the following difference.

E. The optimum and limiting reactions of *Th. thioparus* and *Th. denitrificans* have not been stated, but, from the work of Trautwein, we find that his organism, closely related to the other two forms, has its optimum reaction in the alkaline range (pH = 8.0), and, when grown on slightly acid media, changes the reaction to alkaline. *Th. thiooxidans* grows in a distinctly acid reaction (optimum pH = 3.0) and produces large amounts of acid. The fact that Jacobsen (6) obtained active oxidation of sulfur by means of an organism which was supposed to be the same as Beijerinck's form, would lead to think that he might have had, in addition to that organism, also *Th. thiooxidans* or a closely related strain.

As a matter of fact, this last factor, namely, the question of reaction, could in itself be used as a physiological characteristic for the classification of sulfur bacteria. It would place the optimum activity of the first four groups on the alkaline or neutral side and group 5 on the far acid side.

According to the work carried on at the New Jersey Experiment Stations (9, 16), *Th. thiooxidans* seems to be a distinct species, as far as both morphological and physiological activities are concerned. The other two organisms vary somewhat in their description by the different investigators. Beijerinck (1) stated that *Th. thioparus* is practically undifferentiated morphologically from *Th. denitrificans*. These two organisms were supposed to be about 3μ long and 0.5 to 1μ in diameter; but Lieske and Gehring found *Th. denitrifi-*

cans only 1μ long and Duggeli (2) states that *Th. thioparus* is only 0.3–0.5μ long. While Beijeinck found that his organisms separated sulfur from thiosulfate, Trautwein made a detailed study of a denitrifying organism which is unable to do that. This would simply indicate the fact that various organisms have been studied by various investigators and that we have here more than two organisms. A more detailed comparative study of the various organisms representing these groups is needed. This is also substantiated by the results obtained in our own laboratory on bacteria which oxidize sulfur under alkaline conditions and which will be published in the following paper.

Another important differentiating point between *Th. thiooxidans* and the other two organisms is their viability. The first organism has been kept in pure culture, in liquid media, for over a year, without losing either viability or physiological characteristics; the *Th. thioparus* and *Th. denitrificans* have been reported by Beijerinck (1), Gehring (5) and others to deteriorate rapidly in pure culture. The organism studied by Trautwein (13) can be cultivated in ordinary bouillon and can be kept alive in that medium for many months, without losing its power of sulfur oxidation.

As to the occurrence of these organisms in the soil, Gehring (5) stated that the denitrifying sulfur oxidizing bacteria are present in various soil types, but different soils contain different races of this organism which differ greatly in virulence. Trautwein (13) demonstrated the presence of his organism in the soil, while *Th. thiooxidans* has been isolated by Waksman and Joffe (16) from soil-sulfur composts and was used by Lipman (8) in the inoculation of elementary sulfur for application to soils.

As a result of these comparisons, we find these different forms of sulfur oxidizing organisms and others which will, no doubt, be added to the list require various cultural treatment and methods of study.

The various media used for the isolation of the sulfur oxidizing organisms that are or may become active in the soil, are as follows:

1. Beijerinck (1) medium

Tap water	1000 cc.	NH_4Cl	0.1 gm.
$Na_2S_2O_3$	5.0 gm.	$NaHCO_3$	1.0 gm.
$MgCl_2$	0.1 gm.	Medium unsterilized.	
Na_2HPO_4	0.2 gm.		

2. Jacobsen (5) medium

Distilled water	1000 cc.	$MgCl_2$	0.2 gm.
K_2HPO_4	0.5 gm.	$CaCO_3$ or $MgCO_3$	20.0 gm.
NH_4Cl	0.5 gm.	Precipitated sulfur	10.0 gm.

3. Lieske (7) medium

Distilled water	1000 cc.	KNO_3	5.0 gm.
$Na_2S_2O_3$	5.0 gm.	$NaHCO_3$	1.0 gm.
$MgCl_2$	0.1 gm.	$CaCl_2$, FCl_3	Traces.
K_2HPO_4	0.2 gm.		

4. Trautwein (13) medium

Distilled water	1000 cc.	KNO_3	1.0 gm.
$Na_2S_2O_3$	2.0 gm.	NH_4Cl	0.1 gm.
$MgCl_2$	0.1 gm.	$NaHCO_3$	1.0 gm.
Na_2HPO_4	0.2 gm.		

5. Medium used by author and associates (9)[2]

Distilled water	1000 cc.	$MgSO_4 \cdot 7H_2O$	0.5 gm.
$(NH_4)_2SO_4$	2.0 gm.	$FeSO_4$	0.01 gm.
K_2HPO_4	1.0 gm.	Sulfur	10.0 gm.
KCl	0.5 gm.	$Ca_3(PO_4)_2$	10 0 gm.

6. Modification of medium 5 for Th. thiooxidans[2]
(pH value about 4.0)

Distilled water	1000 cc.	$FeSO_4$	Trace
$(NH_4)_2SO_4$	0.2 gm.	KH_2PO_4	3.0 gm.
$MgSO_4 \cdot 7H_2O$	0.5 gm.	Sulfur	10.0 gm.
$CaCl_2$	0.25 gm.		

7. Second modification of medium 5[2]
(pH value about 3.0)

$(NH_4)_2SO_4$	0.2 gm.	Sulfur	10.0 gm.
$MgSO_4.7H_2O$	0.5 gm.	KH_2PO_4, 1.0 M solution	80 cc.
$FeSO_4$	0.01 gm.	H_3PO_4, 1.0 N solution	20 cc.
$Ca_3(PO_4)_2$	2.5 gm.	Distilled water to make	1000 cc.

8. This medium is the same as 1, with the addition of 1 per cent $CaCO_3$, weighed out separately, or 0.25 gm. $CaCl_2$ per liter

9. Solid agar medium of Beijerinck

Tap water	1000 cc.	NH_4Cl	0.1 gm.
$Na_2S_2O_3$	5.0 gm.	Agar	20.0 gm.
K_2HPO_4	0.1 gm.	With or without 2 per cent $CaCO_3$.	
$NaHCO_3$	0.2 gm.		

Medium 10[3]

Media 1, 2, 3, 4, 8, 9 are used for the study of bacteria that are able to oxidize sulfur under neutral or alkaline conditions. Media 5, 6, 7, for the study of bacteria oxidizing sulfur under acid conditions. As a matter of fact, although *Th. thiooxidans* was isolated by means of medium 5, the other media (6 and 7) which were developed later, were found to give much better results. This is due to two factors: *a*, the initial reaction is more favorable for the growth of the organism, *b*. the large amount of buffer (KH_2PO_4) does not allow the acid formed from the oxidation of sulfur to change rapidly the reaction of the medium to such a degree of acidity as to injure the further development of the bacteria.

[2] The sulfur and the $Ca_3(PO_4)_2$ are weighed out separately into the individual flasks. Media 5, 6, and 7 are sterilized, on 3 consecutive days in flowing steam, for 30 minutes.

[3] After this paper has been submitted for publication, another solid medium has been developed for the growth of *Th. thiooxidans*, consisting of 1000 cc. distilled water, 5 gm. $Na_2S_2O_3$, 0.1 gm. NH_4Cl, 0.25 gm. $CaCl_2$, 3 gm. KH_2PO_4 and 20 gm. agar.

As a starting point for the isolation of the microörganisms that are able to oxidize sulfur both under acid and alkaline conditions, two kinds of compost were used, A. The sulfur-floats-soil compost, developed by Lipman, McLean and associates resulted in the isolation of *Th. thiooxidans* described in detail elsewhere (9, 16) both as to methods of isolation, morphological, cultural and biochemical characteristics. B. The alkali-soil-sulfur compost, which consists in composting black alkali soil, having a pH value of 9.6–9.8, with various amounts of sulfur. This compost gave very good results by the use of media 1, 8, 9. At least two organisms have been obtained which are responsible for the oxidation of sulfur under alkaline conditions. These organisms behave in general like *Th. thioparus* and related forms studied by Nathanson (11) Beijerinck (1), Jacobsen (5, 6) and Trautwein (13). But, in addition to some morphological differences, they also show some distinct physiological differences.

Beijerinck reported that *Th. thioparus* when grown on his medium (1), produces a thick pellicle consisting of sulfur enclosing the bacterial bodies. Trautwein reported that his organism (related to *Th. denitrificans*) does not produce any sulfur from the thiosulfate. In our case, an organism was obtained which readily produces sulfur in the presence of $CaCO_3$, but does not produce any in its absence. The idea suggested itself that this may be the explanation of the difference between Beijerinck's and Trautwein's results. Possibly that the CO_2 produced from the carbonate by the acid formed, interacts with the thiosulfate and gives precipitated sulfur. The cultures from the two liquid media, viz., 1, with the $CaCO_3$, on which sulfur has been precipitated and 2, without the $CaCO_3$, on which no free sulfur was formed, were then transferred upon the solid medium 9, with and without $CaCO_3$. In both cases sulfur was precipitated in the streak when the culture was transferred from flask 1, but no sulfur was precipitated in both cases when culture was transferred from flask 2, indicating that we are probably dealing with two different organisms. The existence of a third organism in the mixture also suggested itself, for reasons stated below. The cultures grown on the liquid were transferred to agar media, back again to liquid media, etc., till the following cultures were obtained:

A. Grew readily on solid and liquid media (1, 8, 9) and precipitated sulfur on these media. On the solid medium, the acid produced from the further oxidation of sulfur, acted upon the $CaCO_3$ (when present) producing a clear zone around the streak. This resembles, then, in biochemical characteristics the Beijerinck organism.

B. Grew on solid and liquid media (1, 8, 9) not producing any precipitated sulfur. It produced, however, enough acid to dissolve the $CaCO_3$, when present, and formed a clear zone around the streak on the plate. This would resemble the organism of Trautwein if not for the fact that our culture made the medium always acid, while Trautwein's culture did not produce any acid but when the medium was slightly acid, it actually changed it to alkaline.

C. Grew on the liquid and solid media (1, 8, 9) without producing any sulfur and any acid.

In the case of organisms A and B, the reaction of the liquid medium was changed from pH 9.2 to pH 6.2 and 5.8, respectively, while the sodium thiosulfate all disappeared from the medium in a period of 20 days at 25°C. In the case of organism C, very little of the thiosulfate was oxidized. The peculiar behavior of these three cultures may be due merely to the fact that we had here mixtures of *Th. thiooxidans* and *Th. thioparus* or a related strain.

A comparative study of the oxidation of sulfur by these organisms in the soil, under acid and alkaline conditions, will be made the subject of the following paper.

SUMMARY

A comparative review is presented of the various microörganisms concerned in the oxidation of sulfur and of those organisms which are or may become active in the soil.

The classification of sulfur bacteria into "true" and "untrue" or "thiosulfate" (thionic acid) bacteria, as suggested by Omelianski is shown to be untenable. If a physiological basis is to be used for the classification of the sulfur bacteria, they should be grouped as sulfide, thiosulfate, and true sulfur bacteria. Another basis for physiological classification would be that of the optimum reaction for the activity of the organisms. They would then be divided into organisms having their optimum under acid and under alkaline or neutral conditions. However, the division into five groups, based on the physiological and morphological characteristics of the organisms is, for the present, the most suitable classification.

The composition of various media used for the study of bacteria oxidizing sulfur under acid and alkaline conditions is given.

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THE EFFECT OF LIMES CONTAINING MAGNESIUM AND CALCIUM UPON THE CHEMICAL COMPOSITION OF THE SOIL AND UPON PLANT BEHAVIOR[1]

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INTRODUCTION

As is shown in the paper of Wheeler and Hartwell (22) and in the résumé of Lipman (10), there are several reasons for the repudiation of the lime and magnesia ratio theory of Loew, as it is generally understood. This hypothesis is constantly recurring because it deals with two substances which are of real interest to agricultural chemists. That calcium and magnesium to some degree and in certain forms and relations are antagonistic has been demonstrated by Loew (12) and others. The idea that they should exist in a special ratio in order that each plant thrive is rather exacting. The researches of Osterhout (16), McCool (15), Gile (3), and True (20) are noteworthy as contributing, in a general way, to this subject. From the work of these men it would seem that the relation between calcium and magnesium as affecting the plant is not a simple one, as supposed by Loew, but an interestingly complex relation which is becoming more thoroughly understood.

The fact that there are large quantities of magnesic limestone in this country makes it important that there should be no unnecessary fears with regard to its use because of the magnesium it contains. It is well known that magnesic and even calcic limes when used in large excess are toxic under certain conditions. On this account it would seem advisable to determine whether magnesic and calcic limes are actually deleterious on different types of soil and in what quantities, in what form, for what plants, and under what conditions. A work so broad as this in short-time experiments can be only approximate and yield hardly more than indications that would be of use to the farmer. Long-time experiments are necessary. The analyses and other data presented in this paper are from plats laid out for experimentation of this nature and, representing the first decade, are necessarily preliminary in some respects.

HISTORY OF THE EXPERIMENT

The soil, a Miami silt loam, is derived from reworked glacial material laid down as a sediment from quiet water under uniform conditions. It is the

[1] Contribution 281 from the Agricultural Experiment Station of the Rhode Island State College, at Kingston.

[2] The agronomical account of this experiment by Dr. Burt L. Hartwell constitutes Bulletin 186 of the Rhode Island Agricultural Experiment Station.

same as that of the permanent fertilizer experiments which are contiguous. The land was in sod from 1889 to 1892. From that time on until 1909, when this experiment was started, the area was uniformly planted to miscellaneous crops. Throughout these periods no manure or lime was added. In 1909 the plats of $\frac{3}{5}$ acre were respectively treated with chemicals in the following forms: a high-calcium hydrated lime, a high-magnesium ground limestone, a high-calcium ground limestone, a high-magnesium hydrated lime. One plat serving as check received no lime. Because of difficulties in obtaining the high-magnesium hydrated lime, it was not applied until the next year, 1910. Two additional applications were made in 1914 and 1916, respectively.

The amounts of plant nutrients with which the plats were dressed have been the same each year for all plats and have been deemed ample for the crop planted. Since 1917, every practical opportunity has been taken to include magnesium in the fertilizers and to reduce the proportion of calcium in them. This has led to the use of double superphosphate and low-grade sulfate of potash. The former has a smaller proportion of calcium to phosphoric acid than most forms of commercial phosphate and the latter contains magnesium. No farm manure has been added.

A CONSIDERATION OF THE LIME MATERIALS APPLIED

In table 1 are given data concerning the lime materials applied. The mechanical analyses of the 1909 samples are not available. It will be seen that the subdivision of the magnesic limestone is much greater than that of the calcic limestone. The calcic and magnesic hydrates possessed the usual pulverulent character of slaked limes. White (23), and later Hartwell and Damon (6), have done work which indicates that limestones on the soils under consideration by them are roughly proportional in their availability over a season or more to the percentage that will pass through an 80- or 100-mesh sieve. On this basis the magnesic limestone would be more active than the calcic limestone.

The chemical and mechanical analyses correspond closely from year to year of application except for the calcic hydrate in the first year, which contained an abnormal quantity of magnesia. This correlation is to be expected, since in most cases they were obtained from the same source each time and the ground stone and analogous hydrated material are from the same quarry.

The percentage of the limes equivalent to calcium oxide was obtained by titration, with methyl orange as an indicator. These data give an idea as to the relative neutralizing value of the limes and is important inasmuch as the limes have been applied in equal neutralizing equivalents. The relative neutralizing power determined on this basis is given in table 1.

In table 2 is given the amount of the various limes soluble in a liter of water when agitated by bubbling through carbon-dioxide gas for the periods stated. Two-hundred cubic centimeters of distilled water and a 5-gm. sample were

used, titrations being made with methyl orange as the indicator and the results calculated to the basis given. In absolute amounts the agreement is not close with the work of other investigators, who, however, used different conditions, or materials of divergent composition. Relatively they are the same in some cases. MacIntire (14), and also Hammett, in unpublished results of this station, found that the magnesic limestone is less soluble in carbonated water than the calcic limestone, which agrees with data presented. The reason for this is probably that there is a greater tendency on the part of the calcic limestone to form a soluble bicarbonate. However, the alkalinity of a distilled water suspension of magnesic limestone is slightly greater than that of

TABLE 1

Data concerning the limes applied

	CALCIC HYDRATE	MAGNESIC LIMESTONE	LCALCIC IMESTONE	MAGNESIC HYDRATE
1909				
CaO (per cent)	61.7	32.4	54.9	45.4
MgO (per cent)	10.1	20.8	1 1.0	33.1
Relative neutralizing power	133	100	6000	160
Amount added (lbs.)	4511	6000	00	3750‡
1914				
CaO (per cent)	73.4	29.7	50.2	47.4
MgO (per cent)	1.0	20.1	2.8	31.7
Relative neutralizing power	133	107	100	165
Through 100-mesh (per cent)	100.0	85.0	61.0	100.0
Amount added (lbs.)	2262*	2820	3000	1819
1916				
CaO (per cent)	65.7	26.5	50.4	42.9
MgO (per cent)	3.9	20.3	4.2	32.5
Relative neutralizing power	145	100	103	168
Through 100-mesh (per cent)	100.0	87.0	57.0	100.0
Amount added (lbs.)	3096†	4500	4348	2676
pH of distilled water suspension*		8.5	8.3	

* Determined by Dr. P. S. Burgess.

† 50 per cent extra to the south half.

‡ Applied in 1910.

calcic limestone, indicating that the former has a larger number of hydroxyl ions available to neutralize soil acidity under such conditions.

From the results obtained, the conclusion seems warranted that the magnesic limestone, although it is more finely divided than the calcic limestone, becomes available more slowly.

The magnesic hydrate is more soluble in carbonated water than the corresponding calcic hydrate. This would be expected if the magnesium hydroxide is converted into the carbonated form which, unlike the magnesic limestone, is quite soluble. The high alkalinity of these hydrate forms just before

carbonation processes take place would suggest application at a considerable time previous to planting. The solubilities of the hydrates, as shown in table 2, are in the same direction as those obtained by MacIntire, who used the pure oxides.

It can be seen from table 1 that the magnesic limes contain relatively large amounts of calcium. Consequently the system of nomenclature adopted in this paper is purely arbitrary.

TABLE 2

Solubility of limes in carbonated water at room temperature

Grams equivalent to CaO dissolved in 1 liter

CONTACT	1914 CALCIC LIMESTONE	1916 CALCIC LIMESTONE	1916 MAGNESIC LIMESTONE	1916 CALCIC HYDRATE	1916 MAGNESIC HYDRATE
hours	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
1	0.360	0.326	0.156	0.554	0.705
2	0.378	0.323	0.158	1.256	3.134
4	0.373		0.180		
16		0.383	0.193	0.918	2.229

REVIEW OF CROP RESULTS

With the many varieties of crops grown no readily apparent differences have been observed beyond those already noticed in connection with acid- and limed-soil studies. No correlation has been brought out by the crop data accumulated that would show a decided superiority of one form of lime over another. This work tends to corroborate the work of Lipman and Blair (11), who find that magnesic limestones are par with calcic limestones, within the limits of their experiments.

The lack of thrift in a few crops of late years accompanied by such signs as chlorosis has led to the conclusion that the liming has reached the limit of its beneficial effect on certain sensitive plants and has begun to be associated with a slightly toxic action.

The crops grown just before and during the time of the analytical work of this paper, with the yields, are shown in table 3.

TABLE 3

Yield per acre of field crops grown during the time of the analytical work, 1919–1921

	EARLY POTATOES (LARGE) 1919	TIMOTHY, REDTOP, ALSIKE AND MEDIUM RED CLOVER		
		Hay 1920	Rowen 1920	Hay 1921
	bushels	*tons*	*tons*	*tons*
Calcic hydrate	152	1.84	0.83	4.43
Magnesic limestone	140	1.88	0.75	4.27
Calcic limestone	140	1.95	0.68	4.20
Magnesic hydrate	162	2.17	0.86	4.24
No lime	136	1.39	0.79	3.20

EXPERIMENTAL METHODS

As previously stated, the plant has failed to show any great differences between the various treatments with soil amendments. Therefore, in order to obtain a more thorough knowledge of conditions, a chemical analysis of the soil was undertaken.

The soil was sampled by means of a soil tube of $1\frac{3}{4}$-inch bore and to the depth of 10 inches in one instance and to 12 inches in all other samplings. The borings were evenly distributed over the plat, avoiding the edges. Twenty borings to each $\frac{1}{15}$ acre plat have been found to represent that area fairly, so this number was taken except in the first set of samples (see table 4). The plats were divided into north and south halves in making borings. Although analytical work was done in some cases on both halves, mostly the determinations from the north halves, which are more uniform, are given in this paper.

The samples of soils from the field were air-dried in subdued light and after they were passed through a 20-mesh sieve the coarse material was discarded.

TABLE 4

A synopsis of samples taken

NUMBER	DATE	DEPTH	BORINGS PER PLAT	REMARKS
		inches		
1*	August 13, 1919	10	12	All plats, ground clear
2	April 26, 1920	12	20	All plats, ground clear
3	August 30, 1920	12	20	Magnesium hydrate, no lime, in stubble
4	November 4, 1920	12	20	All plats, in stubble

* Taken by C. G. Bridge, formerly assistant chemist at the Rhode Island Agricultural Experiment Station.

A sample in some cases was ground to pass a 100-mesh sieve for such determinations as total nitrogen and loss in weight on ignition. No decided advantages were observed to be gained by this extra subdivision. This is due to the fact that there are probably no inclusions of organic matter by the mineral substances present in the soil, which are not reached by the concentrated acid, and to the fact that, if reasonable care is taken, probably an equally representative sample of the coarser soil can be weighed out.

The methods of the Association of Official Agricultural Chemists (1916) for soils were used in making the ordinary determinations. Special methods will be described with the discussion of data obtained thereby.

The object in view in taking 12-inch samples was to get well below the surface soil, which averages about 7 inches. This method allows for future deepening of the soil by light plowing of the subsoil while keeping well within the limits of possible future sampling of the same surface weight for comparative determinations. Moreover, the roots of many plants extend as far down as this; and, in cases of plants like alfalfa, even beyond. It eliminates the

trouble of dealing with two samples, one of the surface soil, and one of the subsoil. This increase of about 5 inches in depth beyond the surface soil, however, results in a marked dilution of some of the constituents of the surface soil, such as nitrogen and organic matter.

MISCELLANEOUS TESTS

In all the samples of soils, the percentage by weight of the soil that would pass through a 20-mesh sieve after air-drying was determined, on an air-dry basis. The figures from this mechanical analysis showed a correlation by half plats in the three different complete sets of samples, indicating that the soil is fairly uniform and that the samples are thus far representative of the half plat. The percentage passing through a 20-mesh sieve averaged about 94 per cent. The fine character of the Miami silt loam becomes apparent at once from these data.

Freezing-point determinations were made on the soils sampled 12 inches deep in April, 1920, from the north halves of the plats. No marked differences were observed between any of the plats under observation. The freezing-point depression, determined from 25 gm. of air-dried soil with 5 cc. of distilled water, is about 0.081°C.

Carbonates were determined in these soils and found to be present in negligible quantity. Only a small amount of carbonates is to be expected, when it is considered that the chemicals were added over 3 years before the taking of the samples.

In the spring of 1920, all the plats were seeded to a mixture of redtop, timothy, and alsike and red clovers. Late in the summer an attempt was made to estimate the relative composition of the flora. Inadvertently the species of clovers and to a lesser extent of the grasses were mixed. From the small amount of data collected, it seemed as if the plants germinated equally well on all plats but that their subsequent development differed. There was a tendency for the redtop to give its best growth on the acid plat, while the timothy did best on the limed areas.

The work was repeated with greater care in the second year of the grasses, namely, 1921. Random samples from about fifteen places, well distributed over the plat, were taken. Each sample had an area of 16 square inches. The plants were dug up by the roots, so that they could be distinguished individually. The timothy was recognized by its basal bulb and the redtop by the absence of the same. The alsike and red clovers were known by the blossom or the characteristic leaf-markings. In case of the timothy and redtop, the number of fruited stalks also was noted.

It seemed from the estimates as if the alsike clover and redtop predominated in numbers and total weight on the acid plat. The alsike clover was about equally developed on all the plats. In competition with timothy and redtop, alsike and red clover thrived about equally well on the limed areas in the

second year of growth. The redtop had more fruited stalks on the acid plat. The reverse was true of the timothy, which had more fruited stalks, greater numbers and a greater total weight, on the limed soils.

All the limed plats were very much alike in general appearance. For this reason, and because they exhibited about the same reaction, only two of the limed plats were sampled.

From the similarity in composition of flora on the limed plats and the marked difference on the acid soil, it would seem that the reaction of the soil is an important factor in a mixed herbage.

TABLE 5

Data concerning the plant population

	REDTOP	ALSIKE CLOVER	TIMOTHY	RED CLOVER
Plants per square yard				
Calcic limestone	618 (208)*	192	866 (501)	142
Magnesic hydrate	826 (367)	173	1026 (659)	108
No lime	982 (466)	319	349 (167)	35
Per cent by numbers				
	per cent	*per cent*	*per cent*	*per cent*
Calcic limestone	34	10	48	8
Magnesic hydrate	39	8	48	5
No lime	58	19	21	2
Weight per square yard†				
	gm.	*gm.*	*gm.*	*gm.*
Calcic limestone	116	167	643	137
Magnesic hydrate	157	167	686	108
No lime	203	243	192	41
Per cent by weight				
	per cent	*per cent*	*per cent*	*per cent*
Calcic limestone	12	16	60	12
Magnesic hydrate	14	15	61	10
No lime	29	37	28	6

* Figures in parentheses are numbers of fruited stalks.

† On the basis of oven-dried material.

The yields of hay and rowen are given in table 3 and the data concerning the plant population are tabulated in table 5.

In the late summer of 1920, after the first cutting of the mixed grasses, there was a noticeably better growth of red clover on the acid plat as compared with the limed areas. This was surprising in view of the fact that it is generally believed that red clover thrives best on soils which are nearer the point of neutrality. This phenomenon was repeated in the second growth of 1921. At that time there were more red clover plants on the acid soil than

on the limed areas. The individual plants from the acid soil, on an average, weighed more by about one-half when dried than those on the limed plats. At the first cutting of 1921, the red clover plants from all plats were of about the same weight, but the limed plats surpassed the unlimed area in point of numbers.

THE LIME REQUIREMENT AND REACTION OF THE SOIL

Lime-requirement determinations were made in the four sets of samples by the Hopkins method given in the Association of Official Agricultural Chemists Methods for 1916. For comparison the requirement was estimated by the Veitch method, see Hill (7), and the Howard method (8) on the samples taken April, 1920. Results giving the need for lime by the well-known Jones procedure were at hand for the year 1914, and represent the condition of the soil just before the second application of amendments.

The Hopkins-method determinations indicate little difference in requirement among the limed plats, but a marked deviation between limed and unlimed areas. As is well recognized, the need for lime given by this method is low.

A much higher requirement is shown in case of the unlimed plat by the Veitch, Howard and Jones methods, which is more in accordance with the facts as they are known. White (24), using the Veitch method in a comprehensive study, finds the average lime requirement of acid soils in Pennsylvania to be about 3000 pounds of calcium carbonate to the acre, which is lower than the need shown by the acid plat. The limed soils showed a neutral, slightly acid or alkaline test by the Veitch method. The results are listed in table 6. The hydrogen-ion concentration determinations on these soils are compatible with the other estimations of acidity.

The Hopkins-method determinations show that there is a seasonal change in acidity on the limed plats which may be attributed to the crop or to the leaching by the heavy midsummer rainfall. The requirements after the crop of potatoes were quite high compared with those determined the following spring. The depths of the samples taken after potatoes differ from subsequent ones by 2 inches of subsoil, but it would hardly seem that this would give rise to the differences obtained. This acidity must be fixed in the air-dry soil because the determinations were made simultaneously, after the taking of the samples. This observation, namely, seasonal fluctuation in reaction of the soil, was corroborated by determinations made on soils sampled August, 1920, where the magnesic-hydrate plat shows a summer increase in acidity. Howard (9) finds a similar variation in the need for lime by soil of this type.

In estimating 0.05*N* acetic acid solubles, the amount of acetic acid absorbed or neutralized by the soil was noted. Twenty cubic centimeters of the acid were titrated before and after extraction of the soil, and the difference between these two figures in cubic centimeters of alkali (approximately 0.08 *N*) is given in table 6. The relative reaction is exhibited and correlates with the determinations of lime requirement.

There are no large differences in acidity which can be assigned to the different kinds of lime. Evidently there is about the same amount of active base in these plats and any differences must be correlated with other factors than the final reaction. This is essentially the experience of Lipman and Blair (11), who, however, worked chiefly with the calcic and magnesic limestones.

ALUMINUM EXTRACTABLE BY SOLVENTS

Many acid soils give up soluble aluminum when treated with potassium-nitrate solution. With this in mind, the soils under examination were extracted with normal potassium-nitrate solution and other solvents to see whether there was any difference in soluble aluminum. The potassium-nitrate extract was obtained from the regular determinations of lime requirement by the Hopkins method. With normal ammonium-chloride solution the same procedure was followed as that used in connection with potassium nitrate.

In treating the soils with carbon dioxide, 50 gm. was used with 250 cc. of distilled water in a Kjeldahl flask and the system maintained saturated under a slight pressure (the acid-column of the Kipp generator) for about 5 days with intermittent shaking and agitation by driving carbondioxide gas through the muddy suspension. The five soils were supplied with carbon-dioxide gas from the same generator. This is essentially the method proposed by Hartwell (4).

Trials were made with acetic acid of varying strength to ascertain a concentration which would be sensitive to differences in soluble aluminum in the soil. Twentieth-normal approached nearest to the requirements. The manipulation used in connection with this acid was as follows: 50 gm. of soil were shaken in an end-over-end shaking machine for 3 hours with 150 cc. of approximately 0.05*N* acetic acid.

Filtrations, in all cases, were made through filter paper and this process was repeated until a clear filtrate was secured. The silica in solution was found to be negligible in most instances. The aluminum and iron were precipitated with dilute ammonia water. The iron present was determined by titration against permanganate, and subtracted from the weight of ignited oxides, in case of the acetic-acid extractions; but this correction was not applied with the other methods of procedure, because the ashed precipitate seemed to be free from iron as indicated by color. At the most the iron extracted was only a small fraction of the aluminum oxide obtained. Tests were made for phosphoric acid with the use of ammonium molybdate, but there was none present.

The data enumerated in table 7 will be discussed bearing in mind the solvents and methods used.

No weighable aluminum oxide was obtained from the limed soils with normal potassium-nitrate and normal ammonium-chloride solutions, nor with saturated carbon-dioxide water. A fair amount was secured from the acid plat

TABLE 6

Lime requirements and reaction of soil in north halves of plats

Requirements in pounds of CaO per acre-foot of 3,000,000 pounds air-dry soil

LIME REQUIREMENT METHODS	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME	DATE SAMPLED	DEPTH TAKEN
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*		*inches*
Jones*	3080	3290	2970	3190	5080	1914	12
Hopkins	80	95	153	105	630	Aug., 1919	10
Hopkins	22	45	35	34	512	Apr., 1920	12
Hopkins				97	473	Aug., 1920	12
Hopkins	21	33	29	22	517	Nov., 1920	12
Howard	3300	3600	3900	3600	5400	Apr., 1920	12
Veitch	Alkaline	Slightly alkaline	Slightly acid	Alkaline	3900	Apr., 1920	12
	pH†	*pH*†	*pH*†	*pH*†	*pH*†		
	7.2	7.2	6.6	7.4	5.2	Nov., 1920	12
	6.6	6.3	6.4	7.1	4.9	May 12, 1920	7‡
	6.3	6.1	6.2	6.4	4.7	July 5, 1920	7‡
	6.3	6.1	6.3	6.6	4.9	Aug. 16, 1921	7‡
Relative 0.05 *N* acetic acid absorption	3.9	4.4	3.9	4.2	1.5	Aug., 1919	10

* Determined by G. E. Merkle.

† Determined by Dr. P. S. Burgess.

‡ Determined on moist soil.

with these solvents. Where 0.05*N* acetic acid was employed a small quantity was brought into solution from the limed plats and a much larger amount from the unlimed soil. There seems to be little variation in the active aluminum attributable to the different types of lime, as revealed by the acetic-acid digestion.

This work differs from that of Spurway (19) who concludes from leaching experiments with distilled water that calcium carbonate tends to bring the aluminum into solution. Perhaps it might be said that applications of calcium carbonate had resulted in leaching out all the soluble aluminum present in the soil. The acetic-acid treatment, as carried out in this work of the writer, indicates that there is readily soluble aluminum at hand but it is evidently held in an insoluble form by the alkalinity of the soil and is brought into solution by the soil acidity.

TABLE 7

Aluminum oxide extracted by solvents from soil in north halves

Parts per million of air-dry soil

SOLVENT	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME	DATE SAMPLED	DEPTH TAKEN
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*		*inches*
Normal potassium nitrate....	None	None	None	None	91	August, 1919	10
Normal potassium nitrate....	None	None	None	None	82	April, 1920	12
Normal potassium nitrate....	None	None	None	None	82	August, 1920	12
Normal potassium nitrate....	None	None	None	None	92	November, 1920	12
Normal ammonium chloride..	Trace	Trace	Trace	Trace	79	April, 1920	12
0.05 *N* acetic acid.....	120	110	150	100	440	August, 1919	10
Carbonated water.....	None	None	None	None	47	April, 1920	12

The evidence put forth shows that with these soils active aluminum is an indicator of sourness. Previous work has demonstrated (5) that aluminum is toxic to certain plants and therefore it is probable that it is one of the causes of the inability of the acid soils of this type to produce satisfactory yields of some crops.

THE CALCIUM AND MAGNESIUM IN THE SOIL

Efforts to ascertain what strength of solvent would bring out these elements in a ratio that might be correlated in some way with the crop response have been more or less futile. In this paper the work of Loew and his associates on this problem has received most attention (12).

Five solvents were used in the present study, as follows: (a), normal ammonium-chloride solution; (b), the saturated carbon-dioxide water, other details of which are given under the heading, "Aluminum oxide extractable by solvents;" (c), the normal potassium-nitrate solution of the Hopkins method; (d), the 10 per cent hydrochloric acid recommended by Loew (12); (e), the hot, strong hydrochloric acid, as used in the Hilgard method. The calcium and

magnesium were determined gravimetrically by well recognized methods of procedure. The results of this work are given in table 8.

In the carbon-dioxide water determinations a larger proportion of CaO than MgO was brought into solution. In the digestion where hot, strong acid was used nearly the reverse is true. This finding would indicate that the magnesium is present in a more difficultly soluble form than the calcium. Apparently there is an abundance of available calcium and magnesium for plant-food even on the sour soil, as shown by solubility in carbonated water. The attack of the cold 10 per cent acid recommended by Loew is about half

TABLE 8

Amounts of CaO and MgO extracted by solvents from the soil in the north halves from 12-inch samples taken April 26, 1920

Parts per million of air-dry soil

	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME
Carbonated water:					
CaO (p.p.m.)	478	357	503	368	172
MgO (p.p.m.)	64	207	77	212	80
Ratio CaO-MgO	7.5–1	1.7–1	6.5–1	1.7–1	2.2–1
Normal ammonium chloride:					
CaO (p.p.m.)	1207	743	.....	796	209
MgO (p.p.m.)	71	262	57	281	31
Ratio, CaO–MgO	17.0–1	2.8–1	.....	2.8–1	6.7–1
Normal potassium nitrate*					
CaO (p.p.m.)	1280	860	1210	780	280
Loew's 10 per cent cold HCl:					
CaO (p.p.m.)	.....	1350	1730	1420	400
MgO (p.p.m)	860	1170	1010	1400	780
Ratio, CaO-MgO	.....	1.2–1	1.7–1	1.0–1	0.51–1
Hilgard's 25 per cent hot HCl:					
CaO (p.p.m.)	4100	2820	3600	3750	2810
MgO (p.p.m.)	3450	3720	3200	4170	3250
Ratio, CaO–MgO	1.2–1	0.76–1	1.1–1	0.90–1	0.87–1

*10-inch sample taken August, 1919.

as vigorous as that of the hot concentrated acid, and in addition a slightly higher proportion of CaO to MgO is removed from the soil.

It is noticeable that the normal potassium-nitrate and normal ammonium-chloride solutions approach the 10 per cent hydrochloric acid (about 3*N*) in their power to extract calcium. This would indicate that there is considerable change of bases, presumably a replacement of the calcium in the zeolitic minerals by potassium and ammonium ions. With the ammonium-chloride reagent the highest proportion of calcium to magnesium is obtained. This is contrary to ideas of some who think that the ammonium chloride might exert a selective action on the magnesium. The amount of magnesium dissolved is about the same as that obtained by the carbon-dioxide treatment,

except on the acid plat, where it is much less, which would make one suspect that the ammonium chloride might be more sensitive to differences in magnesia availability. The presence of a smaller amount on the unlimed plat is in accordance with the work of Lyon (13) who finds that additions of calcium tend to make the magnesium more soluble, as shown by the leachings, and also agrees with the availability as estimated by the soybean (table 9).

The acid plat compares closely in the ratio of soluble MgO to CaO with the soils receiving applications of magnesic limes. The conclusion seems justified that the magnesic limes represent more closely the combination of MgO and CaO which was present in the soil originally, and that the magnesic hydrate is converted into a form similar to that in which the magnesic limestone exists in the soil after application.

THE PLANT AS A LIME-AND-MAGNESIA ANALYST.

Up to this time, several crops had been sampled and analyzed for calcium and magnesium and the ratios of absorption calculated. The data are given in table 9. The yields of plants do not show any marked variation with changes in the ratio of CaO to MgO in the analyses of the dried substance.

It appears that the legumes absorbed a higher ratio of calcium to magnesium than the endive, except on the soils given magnesic limes, where the ratios are about the same.

On the unlimed soil and the plats given calcic limes the percentage of calcium oxide in the plant is usually high compared with the soils treated with magnesic limes. On the other hand, the amount of magnesium oxide absorbed by the plants is highest on the soils receiving magnesic limes. From the fact that the yields are fairly uniform on all plats, it appears that the plants analyzed are able to accommodate themselves without injury within certain limits, to changes in the soil solution. Moreover, luxury consumption of an element when present in excess is not uncommon in the plant kingdom.

Parker and Truog (17) come to the conclusion that there is a close relation between the nitrogen and calcium in plants but not between their contained magnesium and nitrogen. This relation is evident with the majority of plant analyses they considered. The analyses of the plants of this project do not corroborate this theory, where in case of the acid plat the percentage of calcium in the plants is about the same as for the lime-treated soils, but the percentage of nitrogen and magnesium is low in comparison with the limed areas. In the soybean, changes in the absorption of calcium are not paralleled by similar fluctuations in the percentage of nitrogen.

The solvent (referring to tables 7 and 8) that comes nearest to extracting from the soil magnesium and calcium oxides in the ratio in which they are contained by the plants analyzed is the saturated carbon-dioxide water. This solvent would be more appropriate than those more vigorous in their action which are used by Loew and his associates.

TABLE 9*

Calcium and magnesium oxides in plant parts

	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME
Soybean hay, 1913; Whole plat; Analyses on air-dry sample					
Acre yield of hay (tons)	3.76	3.82	3.94	4.06	2.66
CaO (per cent)	1.55	1.40	1.94	1.39	1.58
MgO (per cent)	0.50	0.73	0.37	0.86	0.27
Ratio, CaO–MgO	3.1–1	1.9–1	5.2–1	1.6–1	5.8–1
Nitrogen (per cent)	2.84	3.02	2.98	3.04	2.42
Soybeans for silage, 1914; North halves; Analyses on moisture-free hay; Acre yields are for whole plat					
Acre yield of silage (tons)	7.82	6.86	8.10	10.52	9.34
CaO (per cent)	1.89	2.10	2.52	1.59	2.39
MgO (per cent)	0.60	1.04	0.46	1.21	0.28
Ratio, CaO–MgO	3.2–1	2.0–1	5.5–1	1.3–1	8.5–1
Nitrogen (per cent)	3.49	3.67	3.68	2.96	2.29
Removed per acre:					
CaO (pounds)	96	83	110	69	101
MgO (pounds)	30	41	20	52	12
Nitrogen (pounds)	176	145	161	128	96
Endive, aerial portion, 1917; North half; Analyses on dried sample					
Acre yield, green (tons)	18.62	21.26	24.00	23.81	19.54
CaO (per cent)	1.42	1.25	1.57	1.29	1.48
MgO (per cent)	0.65	0.86	0.52	1.14	0.52
Ratio CaO–MgO	2.2–1	1.5–1	3.0–1	1.1–1	2.8–1
Nitrogen (per cent)	2.41	2.23	2.08	2.35	1.88
Removed (per acre)					
CaO (pounds)	32	33	48	37	38
MgO (pounds)	15	23	16	33	13
Nitrogen (pounds)	55	58	64	68	49
Winter beans, 1917; South half; Analyses on moisture-free leaves					
Acre yield of beans (bushels)	15	19	18	19	19
CaO (per cent)	4.89	.....	.....	4.27	3.45
MgO (per cent)	0.98	.....	.....	2.14	0.80
Ratio, CaO–MgO	5.0–1	.....	.....	2.0–1	4.3–1

* The majority of the analyses in table 9 were made by G. E. Merkle, formerly assistant chemist at the Rhode Island station.

DETERMINATIONS RELATIVE TO NITROGEN AND ORGANIC MATTER.

Most soils are heterogeneous in their nature. Waynick (21) and others have amply demonstrated this by statistical methods. Consequently a person in making determinations on soils, particularly of nitrogen, should not only realize but estimate his probable error, both of sampling in the field and

of analytical work in the laboratory. In this paper percentages are given to the thousandths place and this is further limited by the probable error. The formulas used are taken from Wood and Stratton (25)—probable error of any of a series of results, P. E. $= \pm .67\sqrt{\frac{\Sigma d^2}{n-1}}$; probable error of average of a series of determinations, P. E. $= \pm .67\sqrt{\frac{\Sigma d^2}{n\,(n-1)}}$.

The figures showing the determinations of nitrogen and organic matter are arranged in table 10.

The first set of samples was taken in August, 1919, to the depth of 10 inches, after a crop of early potatoes. Estimations of total nitrogen were made by the Kjeldahl method for soils without modifications (1). The plats limed with calcic and magnesic hydrates have about the same percentage of nitrogen when the probable error is taken into account. The sour soil ranks with the hydrates. The ground magnesic limestone and the corresponding calcic limestone have a slightly higher percentage, with any superiority in favor of the former. The probable error of sampling these soils was not determined, but subsequent work will show that with samples taken 2 inches deeper it is not very great.

The second samples were taken to the depth of 12 inches in April, 1920, after a fall seeding of wheat which was winter-killed, and after the spring fertilizer (containing 20 pounds of nitrogen per acre) was applied. The 2-inch increase has a marked diluting effect and the differences readily visible before are less prominent. There remains an indication that the magnesic limestone is superior in the percentage of total nitrogen, while the other treatments may be considered about alike.

The last samples were obtained in the fall of 1920 after a crop of mixed grasses and were taken to the depth of 12 inches. On looking at table 10, it will be seen that there is a slight difference credited to the magnesic limestone while the other soil treatments leave the soils alike. The slightly lower percentage of all analyses compared with those on soils taken in April may be partly explained by the compactness of the soil. The average weight of 10 borings of the April samples to the same depth, dry soil, was 12.45 pounds as compared with 13.00 pounds for those taken in November. The November samples contained a slightly greater weight per boring and consequently more subsoil than the April samples. This dilution of the surface soil would slightly reduce the percentage of nitrogen. In addition, it may be partly attributed to the taking of the November samples in the grass stubble. If considerable nitrogen is held in the root system, the reduction of the nitrogen percentage in the soil due to greater compactness would be accentuated.

TABLE 10

Determinations relative to nitrogen and organic matter from the north halves on a moisture-free basis

	CALCIC HYDRATE	MAGNESIC LIMESTONE	CALCIC LIMESTONE	MAGNESIC HYDRATE	NO LIME	DATE SAMPLED	DEPTH TAKEN
	per cent	*per cent*	*per cent*	*per cent*	*per cent*		*inches*
Loss-on ignition	5.9	6.8	6.1	5.5	5.8	Aug., 1919	10
Loss-on-ignition	5.4	5.7	5.8	5.3	5.7	Apr., 1920	12
Humus, Rather method	2.56	2.77	2.73	2.43	2.38	Apr., 1920	12
Humus, A.O.A.C. method				2.36	2.42		
Total nitrogen	0.150 ± 0.002	0.188 ± 0.005	0.164 ± 0.002	0.148 ± 0.003	0.144 ± 0.002	Aug., 1919	10
Total nitrogen	0.132 ± 0.004	0.146 ± 0.001	0.139 ± 0.004	0.127 ± 0.004	0.137 ± 0.004	Apr., 1920	12
Total nitrogen				0.123 ± 0.004	0.129 ± 0.004	Aug., 1920	12
Total nitrogen	0.128 ± 0.002	0.132 ± 0.002	0.122 ± 0.002	0.121 ± 0.004	0.124 ± 0.004	Nov., 1920	12

At the time of taking the April samples, duplicates were secured from both the north and the south halves of the magnesic limestone plat. A series of about 12 nitrogen determinations was made on each of these 4 samples. The percentages of nitrogen on a moisture-free basis with the probable error of the average are as follows: north half, 0.146±0.002; 0.149±0.002; south half, 0.129±0.002; 0.137±0.002.

Humus determinations were made by the Rather method (18), which was found to be more accurate, and to consume less time, than the usual procedure where the soil is extracted with ammonia. The estimations of humus and loss on ignition show a slight superiority in content of organic matter in favor of the ground limestones as compared with the hydrates. The loss on ignition figures are accurate to tenths of one per cent.

From a study of the soil nitrogen and organic matter nothing very extraordinary has been observed. It is a little too early, as yet, to state definitely that the magnesic limestone surpasses the other forms in nitrogen accumulation to any economic extent. No decided superiority of the calcic limes is apparent from the analyses under discussion. The findings here also agree with those of Ellett (2), who perceives no difference in the percentage of soil nitrogen outside his limit of error, over a series of years, between an unlimed soil and a soil treated with burnt lime.

SUMMARY AND CONCLUSIONS

1. In 11 years, 3 applications of hydrated magnesic and calcic limes and ground magnesic and calcic limestones, in carefully controlled field experiments, show little difference in crop yields due to the various forms.

2. Hydrated limes and limestones, high in either calcium or magnesium, act about alike as neutralizers of soil acidity when applied in equivalent amounts, as determined by titration.

3. Calcic and magnesic limes have rendered the aluminum of the soil relatively insoluble. Active aluminum was present on the acid plat.

4. Applications of magnesic limes tend to maintain in these soils a ratio of calcium to magnesium similar to that of the unlimed soil.

5. Plants were not influenced by the varying ratios of CaO to MgO, found in this experiment, but were sensitive to soil reaction.

6. Magnesic limestone shows a slight tendency to increase the percentage of total nitrogen in these soils.

7. Hydrated calcic and magnesic limes up to the present time have not caused any reduction in the percentage of nitrogen, but have resulted in a slight decrease in the percentage of organic matter in the soil.

The author is indebted to Dr. Burt L. Hartwell for direction in conducting the problem and to Mr. P. H. Wessels and Dr. P. S. Burgess of the Rhode Island Agricultural Experiment Station for advice and suggestions.

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THE COMPARATIVE AGRICULTURAL VALUE OF INSOLUBLE MINERAL PHOSPHATES OF ALUMINUM, IRON, AND CALCIUM[1]

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INTRODUCTION

"Phosphorus is the only element that must be purchased and returned to the most common soils of the United States. Phosphorus is the key to permanent agriculture on these lands." This statement of C. G. Hopkins (29) emphasizes the extreme importance of the phosphorus problem in modern agriculture; especially at the present time when the seriousness of the world food situation is making an urgent appeal to agriculturists to increase and to maintain permanently the fertility of all tillable soils.

The acute shortage of transportation facilities has placed farmers, not conveniently situated near phosphate-producing centres, at a disadvantage with regard to procuring phosphorus at other than exorbitant prices. This has resulted in a world-wide prospecting for phosphate deposits and has caused considerable speculation as to the feasibility of utilizing iron and aluminum phosphates for agricultural purposes.

In spite of the fact that a considerable amount of work had been done that demonstrates the value of aluminum and iron phosphates, the general belief is that they have little significance from an agricultural point of view. The fact that they are practically useless for acid phosphate manufacture, combined with their low solubility in citric acid and ammonium citrate solutions is probably the main cause for the popular conception of their agricultural value.

There are also numerous statements by eminent scientists scattered throughout the literature in which aluminum and iron phosphates are referred to as being particularly unavailable as plant-food. The fleeting action of super-

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phosphates on soils rich in aluminum and iron oxides, for example, is ascribed to the conversion of this phosphate into aluminum and iron phosphates.

It was the object of the experiments reported in this paper to determine the comparative values of various phosphates of aluminum, iron and calcium which occur in nature, and simultaneously to determine how they are affected by diverse collateral treatments.

REVIEW OF LITERATURE

Some fundamental considerations

A fundamental fact, which has a very important bearing on the phosphate problem in soils was brought to light by the work of Schloesing and Kossovitsch. In 1899, Schloesing (67) demonstrated the fact that plants can obtain their phosphorus from very dilute solutions, solutions containing only 1 to 2 mgm. phosphoric anhydride per liter. This emphasizes the importance of naturally dissolved phosphates in the soil solution for plant nutrition. Kossovitsch (37) repeated these experiments, verified Schloesing's results and showed simultaneously that the relative feeding powers of plants do not rest solely on their ability to utilize the phosphorus occurring in dilute solutions. Flax, when compared with mustard and peas, has but feeble powers to utilize the phosphorus of tricalcium phosphate rock, but was shown to make good growth on a nutrient solution, which contained only 1.3 mgm. of phosphoric anhydride per liter.

From the work of Schloesing one might at first conclude that the plant roots exert a solvent action on phosphates. Sachs (65) in 1860, demonstrated that plants roots were capable of corroding marble plates. In 1896, Czapek (13) conducted extensive investigations to determine whether roots excrete or secrete acids, which might function in dissolving plant-food. Eventually he concluded that carbonic acid was the only acid given off in considerable quantity by live roots of plants. In 1902, Kossovitsch (37) demonstrated clearly that the plant roots themselves and not the nutrient solution were responsible for obtaining phosphorus from phosphorite. The following device was employed by him to determine this factor: Plants were grown in two sets of cylinders. In the one set, sand mixed with tricalcium phosphate was used as a medium for the plants to grow in. Five liters of nutrient solution were passed daily through each cylinder. In the second set, pure sand was used as a medium for growth. As in the above case, five liters of nutrient solution were added daily with the exception that the nutrient solution was first made to pass through another cylinder containing a mixture of quartz sand and tricalcium phosphate and in which no plants were growing. If the nutrient solution acted as a solvent of the phosphate, the plants in the second set of cylinders should have made a fair growth. The plants grew well in the first set and made hardly any growth in the second, proving that if the nutrient solution exerted any solvent action on the tricalcium phosphate, its action was very slight and that the action of the roots themselves was a very much more important factor. In 1911, Prianishnikov (61) made the claim that iron and aluminum phosphates were gradually decomposed by water and that root excretions do not play the important rôle in assimilation of these phosphates that has usually been ascribed to them.

Varying ability of plants to assimilate phosphorus from insoluble phosphates

In 1893, Balentine (3) working at the Maine Agricultural Experiment Station reported that *Graminae* were benefited more by acid phosphate than by redondite and rock phosphate, and that plants of the *Cruciferae* family were especially strong feeders on rock phosphate. Two years later, Merrill and Jordan (42) placed the four botanical families studied in the order given below as regards their foraging powers for insoluble phosphates.

1. *Leguminosae* as represented by peas and clover.
2. *Cruciferae* as represented by turnips and ruta-bagas.
3. *Graminae* as represented by barley and corn.
4. *Solanaceae* as represented by tomatoes and potatoes.

The insoluble phosphates employed in this investigation were Florida rock phosphate, iron phosphate, and aluminum phosphate.

Kossovitsch at various times between 1898 and 1910 made mention in his writings concerning the feeding powers of different species of plants. In 1901 (36), he commented on the strong feeding powers of buckwheat and mustard when grown with phosphorite as a source of phosphorus. In a later publication (39) in which he summarized his work on the utilization of phosphorite by mustard, clover, oats, and flax, he placed these plants in the order in which they are here mentioned as regards their powers to utilize phosphorite. It should be observed that this order is somewhat similar to that put forth by Merrill and Jordan. Kossovitsch (38) also tried to correlate the feeding powers of plants with their ability to excrete carbonic acid, but the difference in the amounts excreted did not justify the drawing of any definite conclusions.

Schreiber (68) experimented with eleven species of the *Graminae*, nine of the *Leguminosae*, three of the *Cruciferae*, and eleven miscellaneous plants. The *Leguminosae*, the *Cruciferae*, and buckwheat utilized mineral phosphates to a considerable extent, whereas the *Graminae*, flax, tobacco, carrots, asparagus, beets, and potatoes showed little solvent powers.

Wheeler and Adams of Rhode Island (82, 83), Prianishnikov (56, 57), Bonomi (5), Gedroits (23), Chirikov (Tschirikov) (11), Semushkin (69), and Söderbaum (72), are among other workers who have drawn attention to the individuality of plants with respect to the topic under discussion. In nearly all these cases, their results agree in a general way with those of Merrill and Jordan. The work of the above investigators will be considered later in connection with another phase of our problem.

Emil Truog (76, 77) has propounded a theory to explain the individuality of plants with regard to their feeding powers. Plants with a high calcium content he stated, have a relatively high feeding power for the phosphorus in phosphorites. For plants with relatively low calcium content, the reverse is true. Clover, alfalfa, peas, buckwheat, and several of the *Cruciferae* have high calcium content and are, therefore, according to this theory, powerful feeders on insoluble phosphates. Corn, rye, oats, wheat, and millet fall in the opposite class. A calcium oxide content of less than 1 per cent may be considered low. In another publication (78), Truog claimed that high internal acidity of roots is accompanied by high feeding powers for calcium. Logically then, plants with roots of high internal acidity are capable of utilizing insoluble phosphates with greater success than plants with roots of relatively lower internal acidity. It is clear that the individuality of the plants is a large factor when the availability of phosphates is being considered.

Effect of soil on availability of insoluble phosphates

In studying this question three characteristics of soil have been considered by workers:

1. Mechanical composition.
2. Amount of organic matter in soil.
3. Reaction of the soil.

It is generally held (41) that it is preferable to use bone meal and basic slag on warm sandy soils. Soluble phosphates are put to better use on heavier clay soils. Wheeler and Adams (83) claimed that the addition of three-fourths to one ton of limestone per acre removes the drawback of using soluble phosphates on light sandy soils. On peat and muck soils, the first applications of soluble phosphates are ineffective, due to their entering into colloidal combinations, but after these demands have been met, their effects are noticeable. Concerning the reaction, predominant opinion asserts that soluble phosphates are employed with the greatest success on calcareous soils (14, 27, 49). Hilgard (27) in his celebrated work,

"Soils," made the following statement, ". . . . in the presence of high lime percentages, relatively low percentages of phosphoric acid and potash may nevertheless prove adequate; while the same or even higher amounts, in the absence of satisfactory lime percentages, prove insufficient for good production." Paturel (49), Deherain (14) and others claimed that unless sufficient lime be present, the phosphoric acid is fixed by aluminum and iron oxides into unavailable combinations. On the other hand, this view appears contradictory to the observations of Schloesing, fils, regarding the solubility of phosphoric acid in the presence of carbonate of lime (66), but natural conditions seem fully to justify Hilgard's conclusions. Numerous investigators found aluminum phosphates to be very beneficial to plant growth provided they were employed on soils well supplied with lime. Results in Maryland (50), France (1), and Rhode Island (82, 83) all show that favorable results with aluminum phosphate have always been obtained when the phosphate is used in connection with lime or on soils naturally calcareous. When tricalcium phosphate is employed, the best immediate results seem to be obtained on soils not saturated with bases (24) or on soils well supplied with organic matter (28, 82).

Effect of nitrogen compounds on availability of insoluble phosphates

Prianishnikov and a large number of other Russian workers have studied very carefully the effect of various nitrogen compounds on the availability of insoluble phosphates. All the results agree in general that ammonium sulfate enhances the availability of insoluble phosphates and that ammonium nitrate likewise increases the availability, but to a lesser extent. Sodium nitrate either has no effect or depresses the availability. Calcium nitrate is similar in its effect to sodium nitrate, but less marked. These results are due to inherent properties of the salts themselves and not to their conversion into other compounds, for example the formation of nitric acid as the result of nitrification of ammonium salts. Kossovitsch (36) was responsible for the classic work in regard to the effect of ammonium salts. In experiments in which the possibility of nitrification being a factor was carefully prevented, he confirmed in all instances the deductions of Prianishnikov. Wheeler and Adams (83) commenting upon Warington's work (81) seem to be of the opinion that with aluminum phosphates results would have been established which would be the reverse of those given above. The fact that nitrification materially affects the availability of insoluble phosphates has been definitely established by the investigations of Hopkins and Whiting (30). Söderbaum (72) checked up Prianishnikov's deductions. He believed that the physiological reaction of the accompanying nitrogenous fertilizer plays an important part, but claimed that other factors, such as kind of plant, soil and other collateral treatments used, may lessen or even reverse the influence of this factor. This point is well brought out by Chirikov (10) who found that when calcium nitrate replaced ammonium sulfate in his buckwheat cultures, the yields were not reduced, but increased. Nedokuchaev (46) working with different crops, oats and flax, reported that yields were lower where calcium nitrate was used in lieu of ammonium sulfate. On the whole Prianishnikov's deductions seem to be accurate, but we should bear in mind that no hard and fast rule can be laid down. In work on the availability of phosfates, the accompanying nitrogenous fertilizer is a factor that must be remembered, especially when we attempt to make generalizations from our results.

Effect of lime on availability of insoluble phosphates

When the effect on the availability of insoluble phosphates was considered, the influence of lime came up for discussion since the reaction of the soil and lime content of the soil are closely interrelated. Some further opinions on the effect of lime follows. Prianishnikov (61) divided the phosphates into two groups; the one, including tricalcium phosphate, bone meal, and phosphorite, consists of those of which the assimilation is markedly reduced by the lime; the other, including acid phosphate (mono- and di-calcium phosphates), Thomas slag,

mono-potassium phosphate, iron phosphate, and aluminum phosphate, consists of those unaffected by the addition of lime or even benefited by it. The studies were made in sand cultures. The crops employed were barley, peas, oats, wheat, and buckwheat. In all cases, however, where ammonium nitrogen was substituted for nitrate nitrogen, liming was beneficial. Shulov (71) in studies similar to those of Prianishnikov, determined that the assimilability of pure ferrous phosphate and vivianite was unaffected by lime; that of tricalcium phosphate, in the forms of bone meal and phosphorite, was adversely affected; and that of superphosphate, precipitated phosphate and Thomas slag was only slightly reduced. Gaither (21) explained the lack of harmful effects of lime upon the availability of soil phosphates as due to its action in replacing iron and aluminum in combination with phosphorus and so rendering the phosphates more soluble. Gaither used 0.2 *N* nitric acid as a solvent for determining available phosphorus. Wheeler and Adams (84) pointed out that, in the phosphate experiments at Rhode Island, iron and aluminum phosphates were more efficient than floats on limed land. This agrees with the findings of Prianishnikov.

Effect of various solvents on the availability of insoluble phosphates

It is beyond the scope of this work to enter into the controversy as to which solvents of phosphates can be used for determining their availability to plants. Some literature which has a bearing on this work is quoted. Risler (64) claimed that carbonic acid has much less solvent action on aluminum and iron phosphates than on calcium phosphates. Wagner (80) and later Storer (73) claimed that alkalies, such as sodium carbonate, ammonium carbonate, etc., can dissolve phosphates of iron and aluminum. Cameron and Bell (9) claimed to have proved that soil phosphates are decomposed or hydrolyzed by water with formation of other phosphates containing relatively more of the base. Zecchini (85) reported that aluminum and iron phosphates are very insoluble except in alkaline solution. Gedroits (22) worked on solubility of phosphates in 2 per cent acetic and citric acids. The relative solubilities in acetic acid were tricalcium phosphate, aluminum phosphate, ferric phosphate, in the order named; in citric acid dicalcium phosphate and aluminum phosphate were equally soluble, ferric phosphate less soluble. In growing plants in sand culture with these phosphates, the aluminum phosphate pots gave the highest yield, tricalcium phosphate was second, and iron phosphate pots a close third. Truog (75) questions the whole idea of employing chemical solvents as a means for determining the availability of different phosphates, basing his deductions on favorable results obtained with phosphates of aluminum and iron, which are, as a general rule, less soluble than calcium phosphate in such solvents. Elliot and Hill (16) had before this arrived at the same conclusions. Fraps (19), on the other hand, proposed 0.2 *N* nitric acid as the solvent to indicate the available supply of phosphorus in the soil. He asserted that in pot experiments, the phosphoric acid removed by the crops is closely related to the quantity of "active" phosphoric acid. "Active" phosphoric acid is defined as that amount which dissolves in 0.2 *N* nitric acid.

Several workers have indicated the value of dehydrating aluminum phosphate to render it more valuable as a fertilizer. The investigators at the Rhode Island Agricultural Experiment Station have always included roasted redondite in their comparative phosphate tests and have drawn attention to the value of dehydration. Morse (44) found that roasting increased the solubility of aluminum phosphate in neutral ammonium citrate, but pot and field tests failed to verify the laboratory indications of availability. Pilon et al (54) described a method for roasting double phosphates of iron and aluminum in order to render the combined phosphoric acid soluble in ammonium citrate. Fraps (20) pointed out that ignition increases the solubility of wavellite, dufrenite, and variscite in 0.2 *N* nitric acid about ten times and makes them almost completely soluble in 12 per cent hydrochloric acid. Peterson (51) conducted similar investigations and showed that heating wavellite for five hours at 200°C. increased the solubility of the phosphoric acid 4 to 50 per cent and heating to 240°C. increased the solubility to 100 per cent. Dufrenite, when heated at 200°C., was but slightly increased in solubility.

Views concerning the comparative availability of phosphates of aluminum, iron and calcium

Below we have simply an enumeration of claims and counter-claims as to the comparative values of aluminum, iron and calcium phosphates. Many of the statements decrying the value of aluminum and iron phosphates were based not on experimental work planned to test this particular point, but were the outcome of efforts to explain puzzling irregularities in the behavior of superphosphates and acid phosphates. Very many workers, too, reported on the topic under discussion as a side issue of a large problem and very often such work failed to effect a fair comparison because the individual phosphates probably display their optimum availability under unlike conditions.

Merrill (43) reported that in most cases crude Florida rock phosphate outyielded Redonda phosphate. Paturel (49) advised that lime be applied to soils high in oxides of aluminum to prevent the fixation of phosphorus by them. Morse (44), as has already been pointed out, studied the solubility of aluminum phosphates and the effect of dehydration of them and showed that, while the solubility in neutral ammonium citrate was greatly increased, field tests failed to demonstrate a resulting increase in availability. Hilgard (27), as quoted in a former paragraph, stated that in the presence of high lime percentages, relatively low percentages of phosphoric acid and potash may nevertheless prove adequate. This seems to indicate that Hilgard preferred calcium and magnesium as carriers of the phosphate in the soil to other bases.

Deherain mentioned an experiment in France in which the action of superphosphates was very fleeting, due, supposedly, to the phosphoric acid passing into combination with iron and aluminum and so rendering the phosphate incapable of use as plant-food. Wheeler and Adams (83) predicted that soluble phosphates were not likely to have as good after effects on unlimed soil rich in iron and aluminum oxides as would bone meal and basic slag for the reason that the phosphoric acid would be fixed as aluminum and iron phosphates, in which forms plants cannot secure it readily. Gaither (21) studying the effect of lime on the solubility of soil constituents declared that lime renders the insoluble phosphates in the soil soluble by replacing iron and aluminum, which are in combination with phosphorus.

Pfeiffer and Blanck (53) analyzed the effect of alumina and silicic acid gels on the assimilation of phosphoric acid by plants and obtained results which showed that both gels reduced yields of plants as well as their phosphoric acid content. The experiment was conducted with sand fertilized with 3 gm. of basic potassium phosphate and soil extract.

Bishop (4) worked with soybeans in pot cultures and concluded that soluble phosphates were not more desirable than Florida soft rock, iron and aluminum phosphates. Balentine (3) and later Merrill and Jordan (42), all of the Maine Agricultural Experiment Station working with sand cultures, found that acid phosphate gave the best returns in all cases and especially with the *Graminae*. Redondite, a phosphate or iron and aluminum, gave better results with *Graminae* than rock phosphate, but in all other cases the reverse was true. In the second report when these investigators worked with a larger variety of plants, they stated that acid phosphate was best, but the insoluble forms were utilized to a considerable extent and that Florida rock phosphate, on the whole, was better than iron and aluminum phosphates, except for barley, corn, turnips, and potato tubers. The plants used in the investigation were peas, clover, turnips, ruta-bagas, barley, corn, tomatoes, and potatoes. Andouard (1) worked with a calcareous soil and deduced that aluminum phosphate was readily available to plants. Burkett (7) obtained very favorable results with raw and roasted redondite. Gedroits (22), in pot culture with soil, declared that aluminum phosphate gave better yields than calcium phosphate and the latter better yields than iron phosphate. Director Patterson (50) of the Maryland Agricultural Experiment Station, made the following statement: "The iron and alumina phosphates proved in all cases to be valuable sources of phosphoric acid, and it would seem that they deserve a higher rank as a fertilizer than that usually accorded them."

Nagaoka (45) employed phosphates on rice fields exhausted by continuous cropping. All the phosphates gave large increases in yield. Table 1 gives the relative yields, double superphosphates being taken as 100.

Bonomi (5), in comparing aluminum phosphate with mineral phosphate, superphosphate, and Thomas slag, reported that aluminum phosphate gave large increases in yield with both clover and wheat, but that superphosphate was always superior to it; spring wheat yields with aluminum phosphate was smaller than those with Thomas slag, but with clover the reverse was true. Elliot and Hill (16) showed that from weights of crops produced in pot experiments, iron and aluminum do not fix phosphoric acid in forms unavailable to plants; as a matter of fact, they claim that iron and aluminum phosphates produce more plant growth than the calcium compounds do. For this reason, they denounced the solvents used by chemists for determining the reversion of phosphates as useless for the purpose.

TABLE 1

Relative yields of rice as influenced by various phosphates (from Nagaoka)

	FIRST YEAR	SECOND YEAR	THIRD YEAR	FOURTH YEAR	AVERAGE
1. Double super phosphate	100	100	100	100	100
2. Ferric phosphate	140	141	399	58	185
3. Ferrous phosphate	87	88	194	44	103
4. Aluminum phosphate	92	145	514	103	216
5. Calcium phosphate	117	110	161	118	127

Shulov (71) worked with vivianite—a ferrous phosphate—a pure ferrous phosphate, aluminum phosphates, tricalcium phosphate, and superphosphates in sand cultures. In all cases, the iron and aluminum phosphates proved highly efficient as fertilizer and increasing amounts of lime up to 1 per cent produced very little depressing effect on their action. Baguley (2) compared normal orthophosphates of calcium, iron and aluminum on oats, peas, and Swedish turnips grown on artificial soil of sand and chalk. As a general rule, iron and aluminum phosphates proved more efficient than calcium phosphates. Peterson and Truog (52), in pot cultural work, demonstrated that freshly precipitated and dried ferric phosphate served as a better source of phosphorus for oats than did rock phosphate, while for rape, the results were exactly the reverse. Truog (75) later made the following statement: "Contrary to the general belief that aluminum and iron phosphates are relatively unavailable to plants, nine out of ten plants tested made better growth on aluminum phosphate than on calcium phosphate, and six better growth on ferric phosphate."

EXPERIMENTAL

These experiments were planned to determine whether or not it is desirable to employ mineral phosphates of aluminum and iron as sources of phosphorus. Studies were made comparing their value as sources of phosphorus with that of calcium phosphate in various forms both natural and artificial. Simultaneously efforts were made to determine what conditions would cause these phosphates to be of the greatest value for crop growth.

Description of materials used

The aluminum phosphates employed were lazulite from near Death Valley, Inyo county, California, wavellite from Cumberland county, Pennsylvania and Saldanha phosphate from the Cape Province in South Africa; the iron

phosphates were dufrenite from near Vesuvius, Rockbridge county, Virginia; and vivianite from Leadville, Colorado; the calcium phosphates were Florida rock and Laingsburg phosphate from the Cape Province, South Africa. Some of the wavellite was obtained from Montgomery county, Arkansas. Besides these phosphates there were also used bonemeal and acid phosphate. In the sand cultures disodium hydrogen phosphate in solution replaced the acid phosphate. Table 2 gives the analyses of the various phosphates.

TABLE 2

Composition of phosphates employed in experiments

KIND OF PHOSPHATE	PHOSPHORUS	ALUMINUM	IRON	CALCIUM
	per cent	*per cent*	*per cent*	*per cent*
Lazulite	13.72	16.20	5 04	0.97
Wavellite	10.04	17.40	2.48	0.23
Saldanha	9.14	16.30	1.61	1.06
Dufrenite	12.07	1.60	40 20	0.11
Vivianite	9.11	1.20	22.40	0.10
Florida hard rock	14.70	4.17	1.53	26.40
Laingsburg	14.01	2.92	2.59	31.90
Bonemeal	12.52	0 00	Trace	27.10
Acid phosphate	7.01	0.81	0.40	14.70

All the aluminum phosphates are basic phosphates, i.e., they have aluminum hydrate associated with the phosphate and all of the phosphates are more or less hydrated. Lazulite has the additional property of being completely insoluble in acids. Hot aqua regia acting on lazulite for an hour fails to dissolve more than a trace of phosphoric acid. Wavellite and Saldanha phos-

TABLE 3

Essential plant-food elements per acre of 2,000,000 pounds of water-free soil or approximately the surface layer of 6⅔ inches over one acre

PLANT FOOD ELEMENTS	BROWN SILT LOAM	YELLOW SILT LOAM
	lbs.	*lbs.*
Phosphorus	1,096	706
Potassium	32,240	29,180
Nitrogen	4,287	1,942
Limestone requirement by Hopkins' method in pounds of $CaCO_3$ per acre	400	2,949

phates dissolve readily in acids. Infrenite is a basic ferric phosphate containing a trace of magnesium. The formula usually ascribed to it by geologists is, $FePO_4 \cdot Fe(OH)_3$. Vivianite crystallizes in the monoclinic form and is a hydrated ferrous phosphate with the formula $Fe_3(PO_4)_2 \cdot 8H_2O$. The Florida hard rock is rather high in aluminum as compared to the usual run of phosphate from this source. The Lainsburg phosphate contains quite an appreciable quantity of calcium carbonate.

The pot cultures were conducted in 1-gallon glazed earthen-ware pots drained by a hole in the bottom of the pot and capable of holding 10 pounds of soil. In most of the soil cultures a light phase of brown silt loam from the University Farm at Urbana, Illinois, was used. As far as is known the soil had never been cultivated and had never received soil treatment of any kind. The soil is known to respond readily to applications of phosphorus. In later experiments a yellow silt loam soil was introduced. This soil came from near Vienna, in Johnson county, Illinois.

In all soil cultures 10 pounds of soil were used per pot and in the sand cultures 12 pounds of sand.

Experiment 1

This experiment was planned to test the comparative effects of the phosphates on crops and the effect of lime and gyspum on their availability.

The experiment was begun in the spring of 1920. Brown silt loam was used and treated as described in table 4.

The pots were planted to buckwheat and annual white sweet clover. All the buckwheat pots were numbered as in table 4; the sweet clover pots were given the same numbers as the buckwheat pots but had "x" prefixed to the number. Each treatment was carried out in duplicate. The planting occurred on February 6, 1920. The sweet clover seed was inoculated. Twenty buckwheat seeds and thirty sweet clover seeds were planted in each pot. After the seeds were up the plants were gradually thinned so that at the end of 4 weeks only the seven strongest buckwheat plants were left in each pot and the ten strongest sweet clover plants in each of the sweet clover pots.

Much cloudy weather was experienced and this combined with the short days made growing conditions in the greenhouse unsatisfactory. It was noticed that the buckwheat especially was looking decidedly poor. In order to insure the elimination of all factors tending toward depression of growth it was thought advisable to start a new series of cultures in which the buckwheat would receive an application of 1.84 gm. of calcium nitrate, the equivalent of 100 pounds of nitrogen to the acre. In all other respects the same plan of treatment was followed, also:

Series 600 corresponded exactly with series 100
Series 700 corresponded exactly with series 200
Series 800 corresponded exactly with series 300
Series 900 corresponded exactly with series 400
Series 1000 corresponded exactly with series 500

In addition, eight control pots were planted to determine the effect of limestone gypsum and calcium nitrate. The treatment applied to these pots and the yields obtained are shown in table 5.

The planting of this series began on February 22, and was completed on February 24.

TABLE 4

Yields of buckwheat and sweet clover grown on brown silt loam soil treated with various phosphates

PHOSPHORUS		TREATMENT*	NUMBER OF POT	YIELD OF BUCKWHEAT			INCREASE OVER CHECK	NUMBER OF POT	YIELD OF SWEET CLOVER			INCREASE OVER CHECK
Source	Amount			First pot	Second pot	Average			First pot	Second pot	Average	
	gm.			*gm.*	*gm.*	*gm.*	*per cent*		*gm.*	*gm.*	*gm.*	*per cent*
		Check	Check	9.2	8.9	9.05		Check	8.9	9.9	9.4	
Lazulite	2.15	Nothing	101A	10.5	10.6	10.55	16.6	x101A	8.8	9.5	9.20	−2.1
		Limestone	102A	11.0	11.8	11.40	25.9	x102A	8.9	8.8	8.85	−5.9
		Gypsum	103A	10.5	10.8	10.65	17.8	x103A	8.0	Lost	8.00	−14.9
		Gypsum and limestone	104A	10.3	11.3	10.80	19.3	x104A	8.4	9.5	8.95	−4.8
Wavellite	2.81	Nothing	101B	12.0	11.8	11.90	31.5	x101B	10.8	11.1	10.95	16.3
		Limestone	102B	14.0	14.7	14.35	58.6	x102B	11.2	11.9	11.55	22.9
		Gypsum	103B	12.6	11.9	12.25	24.3	x103B	10.9	10.7	10.80	14.9
		Gypsum and limestone	104B	14.7	15.0	14.85	64.1	x104B	10.2	12.0	11.10	18.1
Saldanha	3.23	Nothing	101C	11.0	10.6	10.80	19.3	x101C	9.9	9.9	9.9	5.3
		Limestone	102C	13.3	14.0	13.65	50.8	x102C	12.0	12.9	12.45	32.4
		Gypsum	103C	10.8	11.1	10.95	20.9	x103C	10.9	11.7	11.30	2.0
		Gypsum and limestone	104C	13.7	13.4	13.55	49.7	x104C	12.8	13.2	13.00	38.3
Dufrenite	2.44	Nothing	201A	9.5	8.8	9.15	1.1	x201A	9.8	9.2	9.5	1.1
		Limestone	202A	8.6	8.9	8.75	−3.2	x202A	9.1	8.2	8.65	−8.0
		Gypsum	203A	9.8	9.2	9.50	5.0	x203A	10.0	8.8	9.45	0.0
		Gypsum and limestone	204A	7.2	9.8	8.50	−6.1	x204A	8.4	9.9	9.14	−2.8

Vivianite	3.24	Nothing	201B	15.5	15.0	15.25	68.5	x201B	12.0	11.1	11.55	22.9
		Limestone	202B	15.4	13.5	14.45	59.7	x202B	11.8	10.7	11.25	19.7
		Gypsum	203B	14.5	13.4	13.95	54.1	x203B	13.1	11.9	12.50	33.0
		Gypsum and limestone	204B	13.7	13.7	13.70	51.4	x204B	12.1	10.7	11.40	21.3
Florida hard rock	2.01	Nothing	301A	15.0	15.3	15.15	67.4	x301A	13.8	14.9	14.35	52.7
		Limestone	302A	14.9	14.8	14.85	64.1	x302A	15.0	13.7	14.35	52.7
		Gypsum	303A	15.0	14.3	14.65	61.8	x303A	14.6	14.2	14.25	51.6
		Gypsum and limestone	304A	12.3	10.9	11.60	28.2	x304A	13.7	15.0	14.35	52.7
Laingsburg phosphate	2.00	Nothing	301B	15.9	17.0	16.45	81.6	x301B	15.3	13.3	14.30	52.1
		Limestone	302B	13.2	12.3	12.75	40.9	x302B	14.8	15.0	14.90	58.5
		Gypsum	303B	13.9	14.4	14.15	56.3	x303B	13.1	16.5	14.80	57.4
		Gypsum and limestone	304B	12.7	12.9	12.80	41.4	x304B	14.2	15.6	14.90	58.5
Bone meal	2.24	Nothing	401	18.2	17.6	17.90	97.8	x401	15.4	13.7	14.55	54.8
		Limestone	402	16.4	17.2	16.80	85.6	x402	14.7	15.4	15.05	60.1
		Gypsum	403	20.5	18.0	19.25	113.3	x403	14.5	15.9	15.20	61.7
		Gypsum and limestone	404	15.9	16.0	15.95	76.2	x404	13.6	16.0	14.80	57.4
Acid phosphate	3.80	Nothing	501	15.8	17.9	16.85	86.2	x501	15.1	12.9	14.00	48.9
		Limestone	502	16.9	18.4	17.65	95.1	x502	16.0	13.8	14.90	58.5
		Gypsum	503	17.5	19.0	18.50	104.4	x503	15.8	16.6	15.70	67.0
		Gypsum and limestone	504	17.7	18.3	18.00	98.9	x504	14.4	15.7	15.05	60.1

* Each gallon pot exposed a soil surface of approximately $\frac{1}{179,000}$ acre.

Phosphorus was applied at a rate equivalent to 1000 pounds of 65 per cent rock phosphate per acre, i.e., 130 pounds of phosphorus per acre.
Limestone was applied at the rate of 1 ton per acre or 4.35 gm. per pot.
Gypsum was applied at the rate of 200 pounds per acre or 0.45 gm. per pot.

From the third week in February to the end of March good growing weather prevailed. All the plants made good growth. On the following dates the plants were sprayed with nicotine sulfate to kill thrips with which they had become infested: March 7 and 8, April 2, 18 and 19. The spraying on March 7 was done in cloudy weather. The weather, however, suddenly cleared up with the result that some of the plants were injured. "Scald" spots developed on the buckwheat. The 600 series suffered most. On all other occasions spraying was done in the evening. The crops were harvested May 1, preserved in cheesecloth bags until air-dry and weighed.

TABLE 5

Yields of buckwheat on brown silt loam showing the effect of calcium nitrate limestone and gypsum applied singly and in all possible combinations

NUMBER OF POT	TREATMENT	YIELD OF CROP			INCREASE OVER CHECK
		First pot	Second pot	Average	
		gm.	*gm.*	*gm*	*per cent*
1101	Calcium nitrate	10.9	11.7	11.3	28.4
1102	Calcium nitrate, L	11.4	9.9	10.65	22.1
1103	Calcium nitrate, G	11.8	12.0	11.9	35.3
1104	Calcium nitrate, G, L	10.0	10.0	10.0	13.7
1105	L	8.9	8.9	8.9	1.1
1106	G	9.1	8.8	8.95	1.7
1107	G, L	9.4	8.4	8.9	1.1
Check	None	8.7	8.9	8.8	

DISCUSSION AND RESULTS OF EXPERIMENT 1

The relative increase in yield over checks are significant in all cases except perhaps for lazulite and dufrenite. The yields and increases in yields are recorded in tables 4, 5, and 6.

In table 6 the percentage increase over checks was calculated with pot 1101 as the check. From table 5, the effect of limestone, gypsum and calcium nitrate may be determined. Limestone and gypsum had no apparent effect when applied either alone or in combination. Series 100 to 500 inclusive show that on buckwheat, bonemeal and acid phosphate gave the best results. Large increases in yield were obtained with the mineral phosphates of calcium on the unlimed pots and with wavellite and Saldanha on the limed pots. Vivianite gave substantial increases in yield in both the limed and unlimed soil. The yields with Florida phosphate and Laingsburg phosphate on the limed pots showed that the crops were benefited considerably by the addition of the phosphorus. On the unlimed pots small, but probably significant, increases in yield were obtanied where wavellite and Saldanha phosphates were used. Dufrenite and lazulite had little or no effect on the growth of the buckwheat.

From series 600 to 1000, inclusive, the value of calcium nitrate when used in conjunction with the phosphate minerals can be determined. Table 6 shows

TABLE 6

Yields of buckwheat grown on brown silt loam treated with various phosphates together with calcium nitrate

NUMBER OF POT	TREATMENT*	YIELD OF CROPS			INCREASE OVER NO. 1101
		First pot	Second pot	Average	
		gm.	*gm.*	*gm*	*per cent*
601A	Laz.	14.0	13.7	13.85	22.6
602A	Laz., L	16.2	16.1	16.15	42.9
603A	Laz., G	12.8	13.4	13.10	15.9
604A	Laz., G, L	15.4	16.2	15.80	39.8
601B	Wav.	16.8	16.4	16.60	46.9
602B	Wav., L	20.3	21.4	20.85	84.5
603B	Wav., G	15.9	15.7	15.80	39.8
604B	Wav., G, L	19.4	19.0	19.20	69.9
601C	Sal.	16.1	16.6	16.35	44.7
602C	Sal., L	19.5	19.2	19.35	71.2
603C	Sal., G	16.2	15.3	15.75	39.4
604C	Sal., G, L	19.6	18.1	18.85	66.8
701A	Duf.	15.4	14.9	15.15	34.1
702A	Duf., L	16.5	15.2	15.85	40.3
703A	Duf., G	15.8	15.4	15.60	38.1
704A	Duf., G, L	14.3	14.0	14.15	25.2
701B	Viv.	18.6	18.5	18.55	64.1
702B	Viv., L	17.4	18.0	17.70	56.7
703B	Viv., G	17.6	17.9	17.75	57.1
704B	Viv., G, L	20.2	20.2	20.20	78.7
801A	Fl. R.	18.0	20.4	19.20	69.6
802A	Fl. R., L	18.1	17.9	18.00	59.3
803A	Fl. R., G	19.3	20.6	19.95	76.6
804A	Fl. R., G, L	18.0	17.7	17.85	57.9
801B	Lgg.	20.2	20.9	20.55	81.8
802B	Lgg, L	15.6	16.3	15.95	41.1
803B	Lgg., G	21.2	19.9	20.55	81.8
804B	Lgg., G, L	17.0	16.6	16.80	48.7
901	Bone	20.8	19.7	20.25	79.2
902	Bone, L	16.1	17.1	16.60	46.9
903	Bone, G	18.9	17.9	18.40	62.8
904	Bone, G, L	15.8	16.3	16.05	42.0
1001	Ac. P.	18.8	20.1	19.45	72.1
1002	Ac. P., L	19.0	18.7	18.85	66.8
1003	Ac. P., G	17.9	19.6	18.75	65.9
1004	Ac. P., G, L	19.4	19.4	19.40	71.7

*These treatments were identically the same as those given in table 4.

that it enhanced the value of all the phosphates except bonemeal and acid phosphate. Even lazulite and dufrenite in this experiment have benefited the buckwheat considerably. The increases in yield here show that wavellite and Saldanha phosphate on limed soil are on a par with the calcium phosphate minerals on unlimed soil and as good as bonemeal, acid phosphate and vivianite.

With sweet clover different results were obtained. Lazulite and dufrenite again showed no effect. Vivianite gave small but significant increases in yield. On unlimed soil Saldanha phosphate had no effect on crop growth but on the limed soil substantial increases in growth were evident. The best results were obtained with the calcium phosphates. Little difference could be discerned between these phosphates.

It is noticeable that with the aluminum phosphate consistent gains in yield were made by the addition of lime; with the iron phosphate no effect was noticeable, and with calcium phosphates the reverse effect was to be observed. As already pointed out the phosphates of aluminum and iron employed in this experiment are basic phosphates. Aluminum phosphate according to Truog (77) owes its availability to the relative ease with which it hydrolyses in neutral or nearly neutral solutions. From a chemical point of view, this assumption is probably correct. The salt is formed from a strong acid and a weak base and will, therefore, hydrolyze readily according to the following equation:

$$(1)\quad AlPO_4 + 3H_2O \rightleftarrows Al\begin{matrix}OH\\OH\\OH\end{matrix} + H_3PO_4$$

When such a reaction takes place in the presence of plant roots, there will be a tendency for the phosphoric acid to be removed and the aluminum hydrate to remain in the soil. The net result would be that the aluminum phosphate in the soil will become more and more basic. From the law of mass action it is evident that as the phosphate becomes more basic the rate of hydrolysis of the phosphate will diminish. As time goes on plants will experience increasing difficulty to obtain phosphorus as a result of the reaction represented in equation (1). The beneficial action of lime on aluminum is evident from the following reactions:

$$(2)\quad CaCO_3 + H_2CO_3 = CaH_2(CO_3)_2$$
$$(3)\quad 2Al(OH)_3 + 3CaH_2(CO_3)_2 \rightarrow Ca_3Al_2O_6 + 6H_2CO_3$$

The lime therefore removes the aluminum hydrate from the reaction by precipitating it as the very insoluble calcium aluminate. The continual removal of aluminum hydrate prevents reaction (1) from reaching an equilibrium so that plants will be supplied steadily with a supply of soluble phosphorus. The lime may, of course, precipitate the phosphoric acid as tricalcium phos-

phate but such precipitated tricalcium phosphate has repeatedly been shown to be readily available. The phosphorus will become thoroughly disseminated in the soil and furthermore is readily rendered soluble by carbonic acid in the following manner:

$$Ca_3(PO_4)_2 + 2H_2CO_3 \rightarrow Ca_2H_2(PO_4) + CaH_2(CO_3)_2$$

The fact that lime failed to increase the assimilation of ferric phosphate and ferrous phosphate is evident from the above explanation. Iron is a stronger base producing substance than aluminum as is proved by the fact that ferric and ferrous hydrates never behave in the capacity of acids as aluminum hydrate does. Lime, therefore, will have no effect upon ferric or ferrous hydrate. It may be assumed that iron phosphates hydrolyze in the same manner as aluminum phosphates but they are not likely to hydrolyze as readily.

$$(4)\ FePO_4 + 3H_2O \rightleftarrows Fe(OH)_3 + H_3PO_4$$

We would have to conclude, therefore, that as the phosphoric acid is used by the plants the residue will always become increasingly basic and unavailable to plants. Vivianite is a fairly pure ferrous phosphate, $Fe_3(PO_4)_2$; while dufrenite is a basic ferric phosphate, $FePO_4 \cdot Fe(OH)_3$. This probably explains in part the greater availability of vivianite. Probably the utilization of iron phosphates by plants in the soil must be explained as being chiefly due to the action of acids, carbonic acid and nitrous acid, both of which are produced in quantity in soils containing a fair amount of organic matter.

$$(5)\ 2FePO_4 + 3H_2CO_3 \rightarrow 2H_3PO_4 + 2Fe_2(CO_3)$$

The $Fe_2(CO)_3$ is unstable and readily hydrolyzes to give the following:

$$(6)\ Fe_2(CO_3)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2CO_3 \text{ or}$$
$$(7)\ FePO_4 + 3H6\,NO_3 \rightarrow Fe(NO_3)_3 + H_3PO_4$$

Chemically, one would expect that the availability of tricalcium phosphate would be suppressed by the action of limestone. Carbonic acid and nitrous acid produced in soil will react in part at least with the limestone.

$$(8)\ CaCO_3 + H_2CO_3 \rightarrow CaH_2(CO_3)_2$$
$$(9)\ CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2CO_3$$

Apart from this factor the introduction of the common calcium ion will tend to force the equilibrium of the following equation to the left rather than to the right.

$$(10)\ Ca_3(PO_4)_2 + 2H_2CO_3 \rightleftarrows CaH_2(PO_4)_2 + CaH_2(CO_3)_2$$

Truog (77) was able to demonstrate by pot cultures that the introduction of soluble calcium ions into the soil solution tended to lower the rate of assimilation of phosphorus from tricalcium phosphate. This applies especially to plants which do not feed heavily on calcium.

In the literature survey, Hilgard (27) was quoted as stating that in calcareous soils relatively smaller percentages of phosphoric acid will suffice for good plant growth than in acid soils. Truog (77) referring to observations of a decrease in growth of cereals due to the addition of lime carbonate in pot cultures, makes the following statement

"This decrease in availability is undoubtedly due to a condition which is temporary. In becoming acid a soil goes into a condition which takes years to develop, and the addition of lime carbonate causes many profound changes, some of which may affect the availability of the phosphorus. The very favorable results obtained by investigators in long continued field experiments involving the use of ground limestone is strong evidence that any unfavorable result at the start is due to temporary conditions."

If we consider the fact that in a soil, and even a calcareous soil, there is considerably more aluminum, as a rule, than calcium, we cannot but believe that during the ages of weathering to which soils have been subjected, a considerable quantity of phosphorus has gone into combination with aluminum. This phosphorus will be readily available to plants in a calcareous medium as had already been explained. Is it not the aluminum phosphate in the soil rather than the calcium phosphate that has caused Hilgard to express the opinion quoted above? On the other hand, the favorable results obtained in field experiments as the result of long continued use of limestone may be explained in the following manner. Legumes in general grow better in limed soils. Good farm practice would, therefore, result in the incorporation of more organic matter in the soil and especially of more highly nitrogenous organic matter. The limestone creates conditions favorable for biological activity in the soil. The organic matter is more rapidly decomposed and hence there is rapid production of carbon dioxide and nitrous acid. These acids may readily produce acid zones in the soil. In such a heterogeneous mass as the soil, it is not difficult to conceive of acid and alkaline or neutral zones in close proximity. These zones will naturally not be stationary. Acid zones will continuously be formed and again destroyed. In the acid zones, tricalcium phosphate will be dissolved and rendered available to plants; in the alkaline zones, aluminum phosphates will be hydrolyzed and rendered available to crops so that, even there, soluble phosphorus will not be lacking entirely. Lime, as such, undoubtedly reduces the availability of tricalcium phosphate but due to its effect on the organic matter and on the biological activities of the soil, it acts indirectly as a liberator of phosphorus.

Gypsum was added to certain pots in an endeavour to stimulate root growth in the plants and so improve the feeding capacity of the plants. If an increase was to be expected one would have looked for it in connection with the use of aluminum and iron phosphates. With the calcium phosphates, the introduction of the common ion calcium would result in a reduction of yield according to Truog (77). No such reduction can be said to have been observed. The gypsum seems to have been without effect of any kind. It may be pointed out, too, at this time that the choice of calcium nitrate as a nitrogen fertilizer

was probably unfortunate in that it may have caused a reduction in yields on the calcium phosphate pots, due to the introduction of the common ion calcium. On the other hand the Russian work (10) has shown that calcium nitrate is the best form of nitrogen to apply for buckwheat. It is decidedly superior to sodium nitrate. The use of ammonium salts was avoided since it would have introduced the factor of extremely rapid nitrification and the copious production of acids.

Buckwheat and sweet clover were chosen as crops because of their reputation as strong feeders on insoluble phosphates.

Experiment 2

In order to test the various phosphates under conditions where no soil phosphorus was present it was thought advisable to compare their action in sand culture. Buckwheat and sweet clover were again chosen as the crops to be grown. The phosphates, lime and gypsum were applied by thoroughly mixing them in the sand. The rest of the required plant-food nutrients were added in a culture solution composed of 10 cc. of each of the following solutions and the mixture diluted to a liter.

164	gm. of calcium nitrate in	2500 cc.
50	gm. of potassium sulfate in	2500 cc.
20	gm. of magnesium sulfate in	2500 cc.
0.01	gm. of ferric chloride in	2500 cc.

One liter of nutrient solution was added at the time of planting, another liter after 3 weeks, a third liter 2 weeks later, and thenceforth a liter was applied every week. The same pots were employed as in the former experiment and the same quantities of the phosphates, gypsum, and limestone were employed. Each pot contained 12 pounds of sand. The rate of application of fertilizers were therefore:

Phosphates,	1000 pounds of 65 per cent rock phosphate per acre
Gypsum,	200 pounds per acre
Limestone,	1 ton per acre

The fertilizers applied in the solid form were thoroughly incorporated into the sand.

All the pots were planted in duplicate. The sweet clover pots had an "x" prefixed before each number. The buckwheat pots were planted on March 13, 1920, and harvested on May 13. The sweet clover pots were planted on March 13, 1920, and harvested on May 20. Through an error, one of the pots in the buckwheat series did not receive any phosphorus and had to be discarded.

As in the former experiment 30 seeds were planted in each pot, and as time went on the weaker plants were pulled out until finally the buckwheat pots each contained 7 plants and the sweet clover pots each 10 plants.

On April 2, April 23, and May 4, all the pots were sprayed with nicotine sulfate solution to kill thrips with which the plants had become infested.

TABLE 7

Treatments applied to various pots

NUMBER OF POT	TREATMENT IN ADDITION TO NUTRIENTS	NUMBER OF POT	TREATMENT IN ADDITION TO NUTRIENTS
1201A	Laz.*	1041A	Fl., R.
1202A	Laz., L	1042A	Fl. R., L
1203A	Laz., G	1403A	Fl. R., G
1204A	Laz., G, L	1404A	Fl. R., G, L
1201B	Wav.	1401B	Lgg.
1202B	Wav., L	1402B	Lgg., L
1203B	Wav., G	1403B	Lgg, G
1204B	Wav., G, L	1404B	Lgg., G, L
1201C	Sal.	1501	Ac. P.
1202C	Sal., L	1502	Ac. P., L
1203C	Sal., G	1503	Ac. P., G
1204C	Sal., G, L	1504	Ac. P., G, L
1301A	Duf.	1601	Bone
1302A	Duf, L	1602	Bone, L
1303A	Duf., G	1603	Bone, G
1304A	Duf., G, L	1604	Bone, G, L
1301B	Viv.		
1302B	Viv., L		
1303B	Viv., G		
1304B	Viv., G, L		

* For explanation of abbreviations see table 4.

† Included in each liter of nutrient solution at rate of 10 cc. of solution containing 26 gm. Na_2HPO_4 in 2500 cc.

DISCUSSION AND RESULTS OF EXPERIMENT 2

The weights of the crops produced are recorded in tables 8 and 9.

This experiment bears out even more markedly than the former one the relative ability of buckwheat and sweet clover to assimilate phosphorus from the various sources employed. On the unlimed pots bonemeal was on a par in value to disodium hydrogen phosphate in solution. Vivianite proved to be an excellent source of phosphorus. As in the first experiment, the addition of lime and gypsum had no effect on its availability. The average yield from the vivianite pots was equal to the average yield of all the Florida phosphate and Laingsburg pots. On the unlimed pots the tricalcium phosphate minerals proved superior to vivianite; on the limed pots, inferior. In the buckwheat series, wavellite and Saldanha phosphates in the limed pots were on a par with Florida and Laingsburg phosphates in the unlimed pots. In the sweet clover series this does not hold. The sweet clover made considerably better growth with the aluminum phosphates on the limed pots than on the unlimed pots,

TABLE 8

Weights of crops of buckwheat produced in sand culture

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENTS	WEIGHT OF CROP			YIELD
		First pot	Second pot	Average	
		gm.	*gm.*	*gm.*	*per cent* pot 1501 = 100 per cent
1201A	Laz.*	1.20	1.20	1.20	7.8
1201B	Wav.	4.76	5.70	5.23	34.2
1201C	Sal.	5.79	5.09	7.44	48.6
1301A	Duf.	2.26	2.14	2.20	14.4
1301B	Viv.	9.77	9.81	9.79	64.0
1401A	Fl. R.	9.23	9.40	9.32	60.9
1401B	Lgg.	12.66	10.44	11.55	75.6
1501	Ac. P.	14.87	15.72	15.30	100.0
1601	Bone	15.02	15.47	15.25	99.7
					per cent pot 1502 = 100 per cent
1202A	Laz., limestone	1.46	1.38	1.42	9.5
1202B	Wav., limestone	9.45	9.98	9.72	65.1
1202C	Sal., limestone	9.49	8.92	9.21	61.7
1302A	Duf., limestone	2.17	2.26	2.23	14.9
1302B	Viv., limestone	9.42	10.04	9.73	65.2
1402B	Fl. R., limestone	6.39	6.97	6.68	44.7
1402B	Lgg., limestone	6.00	6.73	6.37	42.7
1502	Ac. P., limestone	14.93		14.93	100.0
1602	Bone, limestone	12.19	11.49	11.84	79.9
					per cent pot 1503 = 100 per cent
1203A	Laz., gypsum	1.17	1.23	1.20	8.0
1203B	Wav., gypsum	5.69	6.31	6.00	40.3
1203C	Sal., gypsum	5.63	5.40	5.52	36.9
1303A	Duf., gypsum	2.12	2.28	2.20	14.7
1303B	Viv., gypsum	10.01	9.39	9.70	64.9
1403A	Fl. R., gypsum	10.59	11.03	10.81	72.3
1403B	Lgg., gypsum	10.10	11.50	10.80	72.2
1503	Ac. P., gypsum	14.71	15.18	14.95	100.0
1603	Bone, gypsum	14.37	13.65	14.01	93.6
					per cent pot 1504 = 100 per cent
1204A	Laz., limestone, gypsum	1.39	1.55	1.47	9.6
1204B	Wav., limestone, gypsum	9.47	10.16	9.82	64.4
1204C	Sal., limestone, gypsum	10.37	9.09	9.73	63.8
1304A	Duf., limestone, gypsum	2.01	2.41	2.21	14.5
1304B	Viv., limestone, gypsum	10.40	11.29	10.85	71.2
1404A	Fl. R., limestone, gypsum	6.24	6.73	6.49	42.6
1404B	Lgg., limestone, gypsum	6.16	5.80	5.98	39.2
1504	Ac. P., limestone, gypsum	15.81	14.66	15.24	100.0
1604	Bone, limestone, gypsum	11.60	9.18	10.39	68.2

* For explanation of abbreviations see table 4.

TABLE 9

Weights of crops of sweet clover produced in sand cultures

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENTS	WEIGHT OF CROPS			YIELD
		First pot	Second pot	Average	
		gm.	*gm.*	*gm.*	*per cent* pot x1501 = 100 per cent
x1201A	Laz.*	2.18	2.29	2.24	19.7
x1201B	Wav.	2.51	2.61	2.56	22.5
x1201C	Sal.	2.6	2.86	2.73	24.0
x1301A	Duf.	2.40	2.11	2.31	20.3
x1301B	Viv.	8.53	9.82	9.18	80.8
x1401A	Fl. R.	10.37	10.54	10.46	92.1
x1401B	Lgg.	10.13	10.06	10.15	89.3
x1501	Ac. P.	11.74	10.98	11.36	100.0
x1601	Bone	12.53	13.02	12.78	112.5
					per cent pot x1502 = 100 per cent
x1202A	Laz. limestone	3.01	3.10	3.56	26.6
x1202B	Wav., limestone	6.72	6.50	6.61	49.4
x1202C	Sal., limestone	7.35	7.38	7.37	55.0
x1302A	Duf., limestone	2.26	2.09	2.18	16.3
x1302B	Viv., limestone	9.20	8.41	8.81	65.8
x1402A	Fl. R., limestone	8.63	8.40	8.52	63.6
x1402B	Lgg., limestone	7.31	7.74	7.53	56.2
x1502	Ac. P., limestone	13.42	13.36	13.39	100.0
x1602	Bone, limestone	10.19	10.42	10.31	76.9
					per cent pot x1503 = 100 per cent
x1203A	Laz., gypsum	2.00	1.92	1.96	15.6
x1203B	Wav., gypsum	3.14	2.89	3.02	24.1
x1203C	Sal., gypsum	2.67	2.81	2.74	21.9
x1303A	Duf., gypsum	2.37	2.17	2.27	18.1
x1303B	Viv., gypsum	10.54	9.18	9.86	78.6
x1403A	Fl. R., gypsum	12.04	11.09	11.57	92.3
x1403B	Lgg., gypsum	9.68	9.71	9.70	77.4
x1502	Ac. P., gypsum	12.61	12.47	12.54	100.0
x1602	Bone, gypsum	13.35	12.72	13.04	103.9
					per cent pot x1504 = 100 per cent
x1204A	Laz., limestone, gypsum	2.98	2.89	2.93	21.8
x1204B	Wav., limestone, gypsum	6.71	7.22	6.97	51.9
x1204C	Sal., limestone, gypsum	8.13	8.17	8.15	60.7
x1304A	Duf., limestone, gypsum	2.42	2.27	2.35	17.5
x1304B	Viv., limestone, gypsum	9.79	9.81	9.80	73.0
x1404A	Fl.R., limestone, gypsum	8.86	8.28	8.57	63.9
x1404B	Lgg., limestone, gypsum	6.80	7.45	7.13	53.1
x1504	Ac.P. limestone, gypsum	13.29	13.54	13.42	100.0
x1604	Bone, limestone, gypsum	10.01	10.76	10.39	77.4

* For explanation of abbreviations see Table 4.

but the yields were not as large as those obtained on the unlimed pots fertilized with the tricalcium phosphate minerals. The Florida and Laingsburg phosphates, as with the buckwheat, proved inferior in the limed pots to the same phosphates in the unlimed pots, but in this case equally as good as wavellite and Saldanha on the limed pots. Lazulite and dufrenite behaved as they did in the first experiment, proving themselves poor sources of phosphorus.

A fact to be recorded and probably of some significance is that in the earlier stages of growth of the buckwheat the big differences in total growth on the aluminum phosphate were not so much in evidence. It was during the last 4 or 5 weeks of growth that the plants on the limed pots displayed a greater rate of growth than those on the unlimed pots. Plate 1, figure 1, shows the buckwheat at the age of 6 weeks. The effects of liming is plainly evident where the calcium minerals were applied but not nearly so well marked where aluminum minerals were used. Figure 2 shows that where sweet clover was grown liming showed very marked influence from the very beginning. The pot marked $x1705$ was one of a series that was discarded because of the series becoming infected with red spider. This pot received a complete nutrient solution in which the phosphorus was supplied in the form of monocalcium phosphate. Besides this the pot was limed and treated with 14 gm. of Florida rock phosphate, i.e., rock phosphate at the rate of 7 tons per acre.

These observations tally with the explanation as to assimilability of the phosphates of aluminum and calcium, i.e., in an unlimed medium the availability of aluminum phosphate will decrease as time goes on, whereas the effect of lime on the calcium phosphates will be in evidence immediately. This is considered strong evidence in favor of the explanation as to the effect of lime on the availability of aluminum phosphate.

It is remarkable that similar results have been obtained with buckwheat and sweet clover. Both crops, of course, are known to be heavy feeders on phosphates; but, on the one hand, buckwheat has a rather limited rooting system while sweet clover, on the other hand, has a very extensive rooting system. It seems, therefore, that the two plants should vary considerably in feeding power or else in the manner in which they feed. It is possible to conceive of the idea that the sweet clover may have been injured by aluminum on the aluminum phosphate series. Soluble aluminum in any form would be injurious to sweet clover. This perhaps explains why sweet clover did not respond as well as buckwheat to treatment with aluminum phosphate. Sweet clover roots probably excrete more carbonic acid than do buckwheat roots. Aluminum phosphate is not as readily dissolved by carbonic acid as is tricalcium phosphate. Buckwheat may feed more heavily on phosphorus rendered soluble by hydrolysis by reason of a more rapid removal of phosphorus from the root-hairs to the growing parts of the plant. It must be borne in mind that in these sand cultures, microörganisms do not play the part that they do in soils. None of the pots were inoculated with soil infusion and no nitrifiable material was added. In all probability all pots were infected with

some kind or kinds of organisms but it is not likely that any organisms that could affect the availability of phosphorus appreciably could have been present, or even if they had been present could have exerted any influence, so that the plants had to obtain phosphorus by one of the following methods:

1. The solution of phosphates in the nutrient medium.
2. By hydrolysis and consequent solution of phosphates.
3. By solvent effect of acid root excretions, which would be, according to Czapek (13), chiefly through the agency of carbonic acid.

Phosphorus brought into solution by the first two methods should be equally available to both crops. The phosphorus obtained by the third method would depend on the individuality of the crop in regard to the quantity of the carbonic acid excreted. The differences in feeding power between the two crops under the conditions of the experiment would in all probability have to be ascribed to the rate of carbonic acid excretion, unless there is a difference between the plants in the rate at which phosphorus is translocated from the root hairs to the growing parts of the plants.

It was thought that in sand culture we would be able to duplicate Truog's (77) results with regard to the effect of soluble calcium salts on the availability of the tricalcium phosphate minerals (i.e., reduce it); but gypsum, as in soil cultures, appeared to have no effect on the growth of the plants. It is, of course, possible that due to the large excess of calcium already present in the form of calcium nitrate the additional effect of the calcium ions from the gypsum was too small to register an appreciable difference in crop growth.

Experiment 3

The purpose of this experiment was to determine the effect of nitrification of urea on the availability of the various phosphates both in soil and sand cultures.

The experiment was commenced in the fall of 1920. The media for growth employed were the brown silt loam and the yellow silt loam described in the first section of this paper and pure quartz sand. Throughout the experiment phosphorus and limestone were applied in the same quantities as in former experiments. In the case of the sand cultures the nutrient was applied at the same rate as in previous sand cultures. Where the pots received urea, 0.75 gm. was applied to each pot, i.e., such a quantity was added that, if all the nitrogen in it were converted to nitric acid, enough acid would be formed to displace exactly all the phosphoric acid from the tricalcium phosphate applied to each of the pots treated with it. The pots, which did not receive urea, received an application of 2.05 gm. of calcium nitrate, i.e., nitrogen in equal quantity to that added to the pots receiving urea.

The treatments were applied to all the pots and water added to the optimum amount in each pot. The sand pots each received 50 cc. of a soil infusion. The pots were then left unplanted for 14 days, the object being to allow the urea to be nitrified before the germination of the seed.

TABLE 10

Treatments applied to individual pots

TREATMENT	BROWN SILT LOAM SERIES POT NUMBERS	YELLOW SILT LOAM SERIES POT NUMBERS	SAND CULTURE SERIES POT NUMBERS
Laz., $Ca(NO_3)_2$*	11A	61A	111A
Laz., $Ca(NO_3)_2$, L	12A	62A	112A
Laz., urea	13A	63A	113A
Laz., urea, L	14A	64A	114A
Wav., $Ca(NO_3)_2$	11B	61B	111B
Wav., $Ca(NO_3)_2$, L	12B	62B	112B
Wav., urea	13B	63B	113B
Wav., urea, L	14B	64B	114B
Sal., $Ca(NO_3)_2$	11C	61C	111C
Sal., $Ca(NO_3)_2$, L	12C	62C	112C
Sal., urea	13C	63C	113C
Sal., urea, L	14C	64C	114C
Duf., $Ca(NO_3)_2$	21	71	121
Duf., $Ca(NO_3)_2$, L	22	72	122
Duf., urea	23	73	123
Duf., urea, L	24	74	124
Fl. R., $Ca(NO_3)_2$	31A	81A	131A
Fl. R., $Ca(NO_3)_2$, L	32A	82A	132A
Fl. R., urea	33A	83A	133A
Fl. R., urea, L	34A	84A	134A
Lgg., $Ca(NO_3)_2$	31B	81B	131B
Lgg., $Ca(NO_3)_2$, L	32B	82B	132B
Lgg., urea	33B	83B	133B
Lgg., urea, L	34B	84B	134B
Bone, $Ca(NO_3)_2$	41	91	141
Bone, $Ca(NO_3)_2$, L	42	92	142
Bone, urea	43	93	143
Bone, urea, L	44	94	144
Ac. P., $Ca(NO_3)_2$	51	101	151
Ac. P., $Ca(NO_3)_2$, L	52	102	152
Ac. P., urea	53	103	153
Ac. P., urea, L	54	104	154
$Ca(NO_3)_2$	Check 1	Check 1	
$Ca(NO_3)_2$, L	" 2	" 2	No check
Urea	" 3	" 3	group
Urea, L	" 4	" 4	

* For explanation of abbreviations see table 4.

The materials added to the pots were ground together in a mortar and thoroughly mixed before they were incorporated in the growing media. Thorough mixing of the media and the material was effected.

Five series of pots were used, two containing brown silt loam, one containing yellow silt loam, and two containing sand. For each soil, one series was planted to wheat. The two extra series were planted to annual white sweet clover and each of these pots was numbered the same as its corresponding wheat pot except for an "x" prefixed to the number. The pots in the sand series each received in addition a nutrient solution containing magnesium sulfate, potassium sulfate, and ferric chloride. The concentrations of the salts in this solution, the manner and time of application are exactly as described under experiment 1. The treatments applied to the individual pots in all the series are indicated in table 10.

Sweet clover pots in the first series were planted on October 25 and 26, 1920; the wheat pots, on October 27 and 28, 1920; and a second series of pots containing sand were planted to annual white sweet clover on November 7, 1920.

DISCUSSION AND RESULTS OF EXPERIMENT 3

Due to poor light conditions during the winter months all the plants made very slow growth so that harvesting occurred only toward the middle of March. During the growing season the greenhouses were fumigated on two occasions with "nicofume" to rid the plants of aphis. On three separate occasions spraying with nicotine sulfate was resorted to in order to kill the thrips with which the plants had become infested. The last 6 weeks of the growing periods when the days were becoming longer the plants grew most rapidly. The sweet clover, especially, remained stunted to a considerable extent in the earlier growing period.

On March 4, the wheat on the sand cultures was harvested. On March 13 and 14, the wheat on the soil cultures was harvested and on March 18, all the sweet clover pots were harvested. The crops were kept in paper bags dried in an oven at 105°C. and weighed.

The weights of crops obtained are recorded in tables 11, 12, 13, 14, and 15.

From the above tables the percentage increase in growth as a result of the treatments can be determined. In general, the yields from the pots not treated with urea substantiate the findings of the first experiment with respect to the comparative availability of the various phosphates and the effect of lime on the assimilability of the phosphorus. With wheat, acid phosphate gave easily the best results on both limed and unlimed soil, while wavellite and Saldanha phosphates on limed soil and bonemeal on unlimed soil were second in their effect. Florida rock and Laingsburg phosphates were effective on the unlimed soil but failed to produce much increased growth on the limed pots. The sweet clover yields on the brown silt loam series showed that, even where pots had been limed, the tricalcium phosphates were a better source of phos-

TABLE 11

Weight of wheat from brown silt loam series

POT NUMBER	TREATMENT	YIELD OF CROP			INCREASE OVER CHECK 1	
		First pot	Second pot	Average		
		gm.	*gm.*	*gm.*	*per cent*	
11A		5.63	5.73	5.68	−1.6	
11B	Wav., $Ca(NO_3)_2$	6.68	6.20	6.53	13.2	
11C	Sal., $Ca(NO_3)_2$	7.57	8.42	7.99	38.3	
21	Duf., $Ca(NO_3)_2$	5.67	5.58	5.63	−2.4	
31A	Fl. R., $Ca(NO_3)_2$	8.37	8.92	8.65	49.9	
31B	Lgg., $Ca(NO_3)_2$	8.69	8.31	8.50	47.3	
41	Bone, $Ca(NO_3)_2$	9.57	9.07	9.32	61.5	
51	Ac. P., $Ca(NO_3)_2$	10.72	10.31	10.52	82.3	
Check 1	$Ca(NO_3)_2$ alone	5.73	5.81	5.72		
						INCREASE OVER CHECK 2
						per cent
12A	Laz., $Ca(NO_3)_2$, L	6.32	6.41	6.37	10.4	13.6
12B	Wav. $Ca(NO_3)_2$, L	8.64	9.42	9.03	56.5	61.5
12C	Sal , $Ca(NO_3)_2$, L	8.57	9.42	9.00	56.3	61.0
22	Duf., $Ca(NO_3)_2$, L	5.71	5.46	5.59	−3.1	0
32A	Fl. R., $Ca(NO_3)_2$, L	7.09	7.17	7.13	23.6	27.5
32B	Lgg., $Ca(NO_3)_2$, L	6.23	6.26	6.25	8.3	11.8
42	vone., $Ca(NO_3)_2$, L	8.18	7.84	8.01	38.8	43.3
52	Ac. P., $Ca(NO_3)_2$, L	10.03	10.67	10.35	79.4	85.2
Check 2	$Ca(NO_3)_2$, L	5.71	5.46	5.59	−3.1	
						INCREASE OVER CHECK 3
						per cent
13A	Laz., urea	12.80	13.27	13.04	125.9	25.0
13B	Wav., urea	14.95	14.15	14.55	152.2	39.5
13C	Sal., urea	14.71	15.88	15.30	165.1	46.7
23	Duf., urea	13.69	15.31	14.50	153.2	39.0
33A	Fl. R., urea	20.82	19.70	20.26	251.1	94.2
33B	Lgg., urea	19.68	19.97	19.83	243.7	90.1
43	Bone, urea	18.50	19.82	19.16	232.1	83.7
53	Ac. P, urea	16.41	16.84	16.63	188.2	59.5
Check 3	Urea alone	10.09	10.77	10.43	80.7	
						INCREASE OVER CHECK 4
						per cent
14A	Laz., urea, L	10.73	10.75	10.74	86.3	23.6
14B	Wav., urea, L	10.96	12.00	11.48	98.9	31.9
14C	Sal., urea, L	11.74	12.54	12.14	110.4	39.7
24	Duf., urea, L	12.07	11.42	11.80	104.5	35.7
24A	Fl. R., urea, L	17.76	16.55	17.16	197.4	97.5
34B	Lgg., urea, L	14.80	14.03	14.42	149.9	65.9
44	Bone, urea, L	17.25	16.80	17.03	195.1	95.9
54	Ac. P., urea, L	15.35	15.24	15.30	165.2	76.1
Check 4	Urea, L	8.48	8.89	8.69	50.6	

TABLE 12

Yields of sweet clover from brown silt loam soil series

POT NUMBER	TREATMENT	YIELD OF CROA			INCREASE OVER X CHECK 1	
		First pot	Second pot	Average		
		gm.	*gm.*	*gm.*	*per cent*	
x11A	Laz., $Ca(NO_3)_2$	4.78	4.41	4.60	−3.4	
x11B	Wav., $Ca(NO_3)_2$	5.44	5.70	5.57	17.0	
x11C	Sal., $Ca(NO_3)_2$	4.65	5.48	5.06	6.3	
x21	Duf., $Ca(NO_3)_2$	4.70	5.47	5.09	6.9	
x31A	Fl. R., $Ca(NO_3)_2$	7.93	7.15	7.54	58.4	
x31B	Lgg., $Ca(NO_3)_2$	7.46	7.26	7.36	54.6	
x41	Bone, $Ca(NO_3)_2$	10.57	9.66	10.12	112.6	
x51	Ac. P., $Ca(NO_3)_2$	6.72	7.90	7.31	53.6	
xCheck 1	$Ca(NO_3)_2$, alone	4.80	4.22	4.76		
						INCREASE OVER X CHECK 2
						per cent
x12A	Laz., $Ca(NO_3)_2$, L	5.45	4.95	5.20	9.5	−0.4
x12B	Wav., $Ca(NO_3)_2$, L	6.00	6.46	6.23	30.9	19.3
x12C	Sal., $Ca(NO_3)_2$, L	6.84	6.13	6.49	36.3	24.3
x22	Duf., $Ca(NO_3)_2$, L	5.44	5.31	5.38	13.0	3.1
x32A	Fl. R., $Ca(NO_3)_2$, L	6.68	7.05	6.87	44.3	31.6
x32B	Lgg., $Ca(NO_3)_2$, L	6.70	6.23	6.47	35.9	23.9
x42	Bone, $Ca(NO_3)_2$, L	8.70	7.80	8.25	73.3	58.0
x52	Ac. P., $Ca(NO_3)_2$, L	10.69	9.56	10.13	112.8	94.1
xCheck 2	$Ca(NO_3)_2$, L	5.12	5.32	5.22	9.7	
						INCREASE OVER X CHECK 3
						per cent
x13A	Laz., urea	4.87	4.53	4.70	−1.3	13.3
x13B	Wav., urea	5.62	6.21	5.92	24.4	42.7
x13C	Sal., urea	5.11	5.24	5.18	8.8	27.2
x23	Duf., urea	7.21	6.80	7.01	47.3	68.9
x33A	Fl. R., urea	8.12	8.37	8.25	73.3	98.8
x33B	Lgg., urea	6.24	7.67	6.96	46.2	67.7
x43	Bone, urea	7.33	8.03	7.68	61.3	85.1
x53	Ac. P., urea	7.55	7.23	7.39	55.3	33.3
xCheck 3	Urea alone	4.38	3.92	4.15	−12.8	
						INCREASE OVER X CHECK 4
						per cent
x14A	Laz., urea, L	6.72	5.91	6.41	34.7	19.1
x14B	Wav., urea, L	7.34	6.30	6.82	43.3	26.8
x14C	Sal., urea, L	6.73	6.92	6.83	43.3	26.8
x24	Duf., urea, L	6.24	6.42	6.33	32.9	17.7
x34A	Fl. R., urea, L	9.64	8.99	9.33	96.0	73.4
x34B	Lgg., urea, L	9.67	8.94	9.31	95.6	73.1
x44	Bone, urea, L	9.90	10.86	9.38	97.1	74.4
x54	Ac. P., urea, L	10.89	11.74	11.32	137.8	110.4
xCheck 4	Urea, L.	5.29	5.47	5.38	13.0	

phorus for this plant than aluminum and iron phosphates. The effect of liming was concordant with the former findings; it was in the relative powers of assimilating the various phosphates that the plants differed. Wheat uses aluminum phosphates more readily than does sweet clover. Sweet clover is a heavy

TABLE 13

Yields of wheat from pots in yellow silt loam series. (A large number of crops were lost due to the oven, in which they were being dried, becoming overheated and crops being charred)

POT NUMBER	TREATMENT	YIELD OF CROPS			INCREASE OVER CHECK 1	
		First pot	Second pot	Average		
		gm.	*gm.*	*gm.*	*per cent*	
61A	Laz., $Ca(NO_3)_2$	5.36	4.87	5.12	−1.2	
61B	Wav., $Ca(NO_3)_2$	7.48	7.11	7.30	40.8	
61C	Sal., $Ca(NO_3)_2$	5.87	5.63	5.75	11.0	
81B	Lgg., $Ca(NO_3)_2$	7.23	7.11	7.17	38.4	
Check 1	$Ca(NO_3)_2$, alone	5.18		5.18		
						INCREASE OVER CHECK 2
						per cent
62A	Laz., $Ca(NO_3)_2$, L	6.12	5.85	5.98	15.4	2.9
62B	Wav., $Ca(NO_3)_2$, L	7.37	9.05	8.21	58.5	41.3
62C	Sal., $Ca(NO_3)_2$, L	8.75	8.44	8.60	66.0	48.0
82B	Lgg., $Ca(NO_3)_2$, L	6.40	5.90	6.15	18.7	5.9
Check 2	$Ca(NO_3)_2$, L	5.81		5.81	12.2	
						INCREASE OVER CHECK 3
						per cent
63A	Laz., urea	6.14	6.29	6.22	20.1	0.2
63B	Wav., urea	6.35	6.53	6.44	24.3	3.7
63C	Sal., urea	7.89	10.22	9.06	74.9	45.9
83B	Lgg., urea	9.10	10.07	9.59	85.1	54.4
Check 3	Urea alone	6.21		6.21	20.0	
						INCREASE OVER CHECK 4
						per cent
64A	Laz., urea, L	8.26	7.71	7.99	54.2	30.1
64B	Wav., urea, L	9.69	8.44	9.07	75.1	47.5
64C	Sal., urea, L	10.07	10.35	10.21	97.1	49.8
84B	Lgg., urea, L	8.42	7.97	8.20	58.4	33.5
Check 4	Urea, L	5.92	6.31	6.12	18.1	

feeder on calcium, wheat a light feeder. It is to be expected, therefore, that in the presence of lime or even in the absence of lime sweet clover would be capable of assimilating the phosphorus of tricalcium phosphate more readily than would wheat. Truog (77) is of the opinion that oats feed heavily on the natural phosphates of the soil because of their large fibrous root system.

Wheat, which is very similar to oats in its general structure and manner of feeding, should therefore also feed heavily on soil phosphorus. The results of

TABLE 14

Yields of wheat from pots in the sand series

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENT SOLUTION	YIELD OF CROP		
		First pot	Second pot	Average
		gm.	*gm.*	*gm.*
111A	Laz., $Ca(NO_3)_2$	1.90	1.28	1.59
111B	Wav., $Ca(NO_3)_2$	3.66	4.05	3.86
111C	Sal., $Ca(NO_3)_2$	3.16	2.22	2.69
121	Duf., $Ca(NO_3)_2$	1.72	2.04	1.88
131A	Fl. R., $Ca(NO_3)_2$	2.00	1.95	1.98
131B	Lgg., $Ca(NO_3)_2$	2.18	2.07	2.13
141	Bone, $Ca(NO_3)_2$	3.11	2.26	2.69
151	Ac. P., $Ca(NO_3)_2$	10.04	20.21	19.63
112A	Laz., $Ca(NO_3)_2$, L	1.53	1.31	1.42
112B	Wav., $Ca(NO_3)_2$, L	5.40	5.01	5.21
112C	Sal., $Ca(NO_3)_2$, L	4.06	4.16	4.11
122	Duf., $Ca(NO_3)_2$, L	2.23	2.04	2.14
132A	Fl. R., $Ca(NO_3)_2$, L	1.65	1.54	1.60
132B	Lgg., $Ca(NO_3)_2$, L	2.30	2.12	2.21
142	Bone, $Ca(NO_3)_2$, L	2.38	2.16	2.27
152	Ac. P., $Ca(NO_3)_2$, L	17.62	19.40	18.51
113A	Laz., urea	1.60	2.10	1.85
113B	Wav., urea	4.89	5.21	5.05
113C	Sal., urea	6.01	6.00	6.01
123	Duf., urea	2.46	2.67	2.57
133A	Fl. R., urea	4.30	5.44	4.87
133B	Lgg., urea	4.19	3.90	4.05
143	Bone, urea	7.58		7.58*
153	Ac. P., urea	19.34	20.02	19.68
114A	Laz., urea, L	1.90	1.25	1.58
114B	Wav., urea, L	4.77	5.02	4.90
114C	Sal., urea, L	6.20	6.25	6.23
124	Duf., urea, L	1.64	2.00	1.82
134A	Fl. R., urea, L		2.22	2.22*
134B	Lgg., urea, L	2.40	2.30	2.35
144	Bone, urea, L	2.68		2.68*
154	Ac. P., urea, L	19.59	19.97	19.78

* Weights from only one pot available. The duplicate plants had died soon after germination, presumably from the toxic effect of either the urea or ammonia formed from it.

the above experiments justify his conclusions, for the wheat grown in sand culture made but poor growth. On the other hand, the wheat has responded very markedly to phosphate treatment on the soils. It seems logical to be-

lieve that the more rapid development of a root system in the soil due to the presence of some readily available phosphorus accounts for the greater ability

TABLE 15

Yields of sweet clover from the sand series

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENT SOLUTION	YIELD OF CROP		
		First pot	Second pot	Average
		gm.	*gm.*	*gm.*
x111A	Laz., $Ca(NO_3)_2$	0.84	0.53	0.69
x111B	Wav., $Ca(NO_3)_2$	4.00	5.20	4.60
x111C	Sal., $Ca(NO_3)_2$	5.26	5.53	5.40
x121	Duf., $Ca(NO_3)_2$	1.33	1.03	1.18
x131A	Fl. R., $Ca(NO_3)_2$	7.86	10.23	9.05
x131B	Lgg., $Ca(NO_3)_2$	9.90	9.73	9.82
x141	Bone, $Ca(NO_3)_2$	10.27	9.97	10.12
x151	Ac. P., $Ca(NO_3)_2$	11.46	10.17	10.82
x112A	Laz., $Ca(NO_3)_2$, L	1.19	1.14	1.17
x112B	Wav., $Ca(NO_3)_2$, L	6.22	6.10	6.16
x112C	Sal., $Ca(NO_3)_2$, L	6.20	7.93	7.07
x122	Duf., $Ca(NO_3)_2$, L	1.00	1.03	1.02
x132A	Fl. R., $Ca(NO_3)_2$, L	8.23	9.35	8.79
x132B	Lgg., $Ca(NO_3)_2$, L	7.73	7.05	7.39
x142	Bone, $Ca(NO_3)_2$, L	7.20	7.04	7.12
x152	Ac. P., $Ca(NO_3)_2$, L	11.57	10.84	11.21
x113A	Laz., urea	0.48*	0.12*	
x113B	Wav., urea	0.56*	0.77*	
x113C	Sal., urea	*	*	
x123	Duf., urea	*	*	
x133A	Fl. R., urea	7.62	*	
x133B	Lgg., urea	8.45	9.39	8.92
x143	Bone, urea	10.49	*	10.49†
x153	Ac. P., urea	7.42	4.32*	7.42†
x114A	Laz., urea, L	1.12	1.43	1.28
x114B	Wav., urea, L	3.24	3.54	3.39
x114C	Sal., urea, L	4.84	5.46	5.15
x124	Duf., urea, L	*	1.79	1.79†
x134A	Fl. R., urea, L	*	*	
x134B	Lgg., urea, L	9.27	8.04	8.66
x144	Bone, urea, L	8.38	*	8.38†
x154	Ac. P., urea, L	11.70	10.92	11.31

* Part or all of plants died within first 3 weeks.

† From one pot only.

to use phosphorus applied to soil. The poor growth in sand cultures, where only insoluble mineral phosphates are present, is due to the inability to develop a root system in the early growth stages. Sweet clover, with its high

feeding capacity for calcium, finds enough phosphorus in early stages of growth to develop an extensive root system; and, therefore, in later stages is better equipped to forage for its phosphorus. Sweet clover, of course, always has a very much more extensive root system than wheat. The comparison would be more plain if we could compare buckwheat and wheat. It must be borne in mind, however, that the application of calcium nitrate may have reduced the availability of phosphorus for wheat more than for clover, which is capable of utilizing more calcium. It would be interesting to grow wheat in sand culture with insoluble phosphates and supplying it with a very small quantity of soluble phosphorus just after the germination of the plants.

THE ACTION OF UREA

Some remarkable results have been obtained as a result of the action of urea. The object of the addition of urea was to determine the effect of nitrification on the availability of the phosphates. It was an ideal source of organic matter to use because of its being free from phosphorus and convertible only into nitrous (or nitric) and carbonic acids, thus leaving no mineral residue in the soil. Furthermore, urea is nitrified very rapidly. The urea is converted into ammonium carbonate by the urea organisms present in most soils. The ammonium carbonate is rapidly transformed into nitrous acid and carbonic acid. On the brown silt loam where urea was used without phosphate treatment very curious results were obtained. With wheat, very large increases in growth were evident, more in the unlimed pots than in the limed ones. With sweet clover, urea had practically no effect, while on the yellow silt loam series the effect of urea was small. It is evident that in the brown silt loam the acid production as a result of nitrification resulted in the liberation of a considerable quantity of plant food. The reduction in yield of wheat where lime too was applied lends strength to this statement. The failure of response by sweet clover is the result of toxic effect on the plants by the acids produced. The lesser effect of urea on wheat in yellow silt loam series is due to the poor quality of the soil and the inability of the soil to nitrify the urea as rapidly as the brown silt loam did. There is even a possibility that the urea remained unchanged in the soil long enough to injure the young wheat seedlings. No such injury was visible at any time, however.

THE EFFECT OF THE UREA ON THE AVAILABILITY OF THE PHOSPHATES

The effect of the urea on the availability of the phosphates themselves was very remarkable. In many instances yields were almost trebled. Wheat benefited considerably more than sweet clover. The increases in yield due to various treatments are recorded in tables 11, 12, and 13. It is evident that urea exerted its greatest influence on the tricalcium phosphates. Where sweet clover was grown, no, or only small, increases were observed with aluminum phosphates. On the yellow silt loam series, lazulite was the only

aluminum phosphate which benefited by the presence of the urea. An outstanding feature is the remarkable benefit derived by sweet clover from urea and dufrenite in the unlimed series, especially as dufrenite has proved to be a poor source of phosphorus thus far. The last column on the right of tables 11, 12, and 13 give the increases in yield that may be ascribed as due to the phosphorus alone. It is very doubtful whether the figures can be said to represent the influence of the phosphates because the factors regulating growth are much too intricate to be separated in such an arbitrary fashion; but at the same time they show the percentage increase of growth as due to combined efforts of the urea and phosphates as against the influence of the urea or the calcium nitrate.

Plate 2 shows photographs of the various wheat pots which give a clear picture of the effect of the various treatments. The tremendous increase in growth can only be ascribed to the ability of the urea to render plant food available as a result of its transformation into acids. The small quantity of soil in each pot and hence the relatively small quantity of available plant-food in each pot combined with the large number of plants growing in each pot made it difficult for the plants to grow to any considerable size without the addition of fertilizing materials. The roots made a tangled mass in the soil penetrating into every nook and corner of the pots. Hopkins and Whiting (30) showed that nitrite bacteria could dissolve seven times as much phosphorus from rock phosphate as would be required by a growing plant in a medium where this phosphate was the only supply of a base. The urea was in intimate contact with the phosphorus and, therefore, admirably situated for the acids produced to act on the phosphates, rather than on other soil materials. All the pots were well stocked with nitrogen. It is evident then that in the pots not treated with urea the plants suffered from phosphate starvation, while in the pots treated with urea, phosphorus was dissolved in plenty and the extensive network of roots in the pots ensured the utilization of a large proportion of the phosphorus thus placed at the disposal of the plants. An observation which lends support to this is the fact that the wheat, growing on the urea-treated pots, developed heads and seed, while only in isolated cases did any of the heads develop at all on any of the other pots. Seed production and early maturity are coupled with good phosphorus supply. The depression in yields where lime was used together with urea and phosphate and especially tricalcium phosphates, must be explained as due to the neutralization by the lime of part of the acids formed.

The smaller response to urea by aluminum phosphate is probably due to the fact that aluminum is a questionable base for the nitrifying organisms which are known to respond to calcium and magnesium as bases.

In the sweet clover series the formation of soluble aluminum salts was in all probability detrimental to the plants to which they are known to be very toxic. The difference in yield between check 3 and check 4 in table 12 is large enough to conclude that urea alone had injured the plants but that in the pres-

ence of lime it was beneficial. The results from the sand series bear out the above statements. Urea without lime benefited the wheat by supplying at least some soluble phosphorus; on the limed pots the solvent action of the acids was removed so that the calcium phosphates showed hardly any benefit from the addition of urea, but with the aluminum phosphates the lime rendered the aluminum phosphates available so that but small differences were noticeable. Wheat is not so susceptible to the toxic action of aluminum salts of acidity. In the sweet clover series urea and phosphate without lime caused havoc amongst the plants. All the pots treated with aluminum phosphate had their plants severely injured or killed. Even some pots in limed series suffered. This points strongly in the direction that sweet clover was injured by soluble aluminum salts or by acids, or by ammonium or ammonium nitrite.

NITROGEN AND PHOSPHORUS CONTENT WITH AND WITHOUT UREA

The analyses of some of the crops grown in this experiment (table 16) indicate that the differences in growth are due to the supply of available phos-

TABLE 16

Analyses of wheat from sand series

POT NUMBER	TREATMENT	NITROGEN	PHOSPHORUS
		per cent	*per cent*
111C	Sal., $Ca(NO_3)_2$	2.37	0.048
112C	Sal., $Ca(NO_3)_2$, L	2.03	0.054
113C	Sal., urea	2.42	0.076
114C	Sal., urea, L	2.23	0.056
131B	Lgg., $Ca(NO_3)_2$	1.96	0.046
132B	Lgg., $Ca(NO_3)_2$, L	2.04	0.047
133B	Lgg., urea	2.12	0.057
134B	Lgg., urea, L	1.95	0.047
141	Bone, $Ca(NO_3)_2$	2.01	0.048
142	Bone, $Ca(NO_3)_2$, L	2.02	0.050
143	Bone, urea	2.03	0.059
144	Bone, urea, L	2.03	0.046

phorus rather than to any other causes. The analyses were of wheat grown in the sand series—both nitrogen and phosphorus content were determined.

Experiment 4

The purpose of this experiment was to determine the availability of chemically pure phosphates of aluminum, iron, and calcium and the effect of ignition on the availability of mineral phosphates of calcium, iron, and aluminum.

In the first part of the experiment, the chemically pure phosphates were compared, with and without the effect of lime, and in order to insure that the calcium phosphate was not placed at a disadvantage by the use of calcium nitrate, comparative pots were planted in which ammonium sulfate was used

as a source of nitrogen. With the aluminum and iron phosphates a small quantity of calcium silicate was added as a source of calcium where ammonium sulfate was used.

TABLE 17

Yields of buckwheat on pots with chemically pure phosphates and ignited mineral phosphates

POT NUMBER	TREATMENT IN ADDITION TO NUTRIENT SOLUTION	WEIGHT OF CROP		
		First pot	Second pot	Average
		gm.	*gm.*	*gm*
1	Al. P., $(NH_4)_2SO_4$,$CaSiO_3$	3.00	3.30	3.15
2	Al. P., $(NH_4)_2SO_4$, L,$CaSiO_3$.	4.67	4.64	4.66
3	Al. P., $Ca(NO_3)_2$	6.20	6.63	6.42
4	Al. P., $Ca(NO_3)_2$, L	6.92	7.00	6.96
11	Fe. P., $(NH_4)_2SO_4$,$CaSiO_3$	4.47	4.55	4.51
12	Fe. P., $(NH_4)_2SO_4$, L,$CaSiO_3$	4.71	4.35	4.53
13	Fe. P., $Ca(NO_3)_2$	5.39	6.20	5.80
14	Fe. P., $Ca(NO_3)_2$, L	6.27	5.67	5.97
21	Ca. P., $(NH_4)_2SO_4$	4.31	4.25	4.28
22	Ca. P., $(NH_4)_2SO_4$, L	3.16	3.18	3.17
23	Ca. P., $Ca(NO_3)_2$	6.65	6.92	6.79
24	Ca. P., $Ca(NO_3)_2$, L	4.51	4.83	4.67
31	Laz. I., $Ca(NO_3)_2$	3.33	3.65	3.49
32	Laz. I., $Ca(NO_3)_2$, L	4.76	4.70	4.73
33	Laz., $Ca(NO_3)_2$	1.56	1.40	1.48
34	Laz., $Ca(NO_3)_2$, L	2.14	2.57	2.36
41	Wav. I., $Ca(NO_3)_2$	5.96	5.87	5.92
42	Wav. I., $Ca(NO_3)_2$, L	7.49	8.05	7.77
43	Wav., $Ca(NO_3)_2$	2.80	2.47	2.64
44	Wav., $Ca(NO_3)_2$, L	3.59	3.18	3.39
51	Sal. I., $Ca(NO_3)_2$	5.93	6.06	6.00
52	Sal. I., $Ca(NO_3)_2$, L	7.89	7.87	7.88
53	Sal., $Ca(NO_3)_2$	3.03	3.50	3.27
54	Sal., $Ca(NO_3)_2$, L	4.95	4.04	4.50
61	Duf. I., $Ca(NO_3)_2$	2.24	2.29	2.27
62	Duf. I., $Ca(NO_3)_2$ L	2.00	2.29	2.15
63	Duf., $Ca(NO_3)_2$	1.40	1.86	1.63
64	Duf., $Ca(NO_3)_2$, L	1.60	1.76	1.68
71	Fl. R. I., $Ca(NO_3)_2$	6.31	5.96	6.14
72	Fl. R. I., $Ca(NO_3)_2$, L	4.80	4.56	4.68
73	Fl. R., $Ca(NO_3)_2$	6.11	6.21	6.16
74	Fl. R., $Ca(NO_3)_2$, L	4.48	4.77	4.63

* *Key to Abbreviations:* Al. P., Aluminum phosphate; Fe. P., pure ferric phosphate; l., ignited.

The medium used was pure quartz sand which received the same nutrient solution at the same intervals as described in experiment 3. The limestone and other salts were applied in the same manner and quantities as in the former experiments.

These pots were planted on January 17, 1920, and harvested March 29. On three separate occasions the plants were dusted with tobacco dust to control the thrips with which they had become infested. The buckwheat plants were thinned until 6 remained in each pot.

The crops, when harvested, were placed in paper bags, dried in an oven at 105°C., and weighed. Table 17 gives the weights of crops obtained.

DISCUSSION AND RESULTS OF EXPERIMENT 4

The weights of crops obtained are well in accord with what one might expect from the results of experiment 1. Calcium nitrate is evidently a far better form of nitrogen for buckwheat than is ammonium sulfate. Even with calcium phosphate, calcium nitrate proved to be the better form of nitrogen in spite of the fact that ammonium sulfate is supposed to enhance the assimilability of tricalcium phosphates. It is fortunate that calcium nitrate was chosen for the latter half of the experiment as a source of nitrogen. Of the pure phosphates, we may safely state aluminum phosphate is as available as calcium phosphate and that these two are only slightly superior to ferric phosphate as a source of phosphorus for buckwheat. The effect of lime on the availability of the pure aluminum phosphate was not so much in evidence as it was with the mineral phosphates of aluminum. This is to be expected. The aluminum phosphate is free to hydrolyze readily at the beginning, having no aluminum hydrate associated with it. Only as time goes on and the aluminum hydrate begins to accumulate does the lime exert its influence on the availability of the phosphates. With iron and calcium phosphates the effect of lime resulted as expected. The slight effect of lime on pure aluminum phosphate, the failure to affect ferric phosphate at all and the great depression in availability of pure tricalcium phosphate is cited again as strong evidence in support of the theory described under the first experiment as to the effect of lime on the availability of aluminum, iron, and calcium phosphates.

In connection with the relative availabilities of the three types of phosphates to crops, it must be borne in mind that a plant with great ability to utilize tricalcium phosphate was employed, as has been demonstrated time and again. It is very probable that had wheat, oats, millet, flax, or some such low-feeding-power plant been used instead of buckwheat, aluminum and iron phosphates would have shown up to better advantage since their phosphorus is rendered available more readily by hydrolysis than by the action of roots through the agency of carbonic acid. Acids have less solvent action on aluminum and iron phosphates than on calcium phosphates as has been demonstrated in experiment 3.

Ignition of the phosphates has had a remarkable effect on the assimilability of the phosphorus. It may be stated here that the phosphates were ignited at a bright red heat for 5 hours. Saldanha phosphate and wavellite lost about 15 per cent of their weight; the other three phosphates about 5

per cent. This loss of weight was, of course, taken into account when applying the phosphates so that all phosphates were applied on an equal phosphorus basis. Ignition of the three aluminum phosphate minerals resulted in doubling the crops obtained with them as compared with the unignited minerals. Smaller but still significant increases in yields were realized by igniting dufrenite. Ignition has had no influence on the availability of the calcium phosphate used.

The increased availability of the aluminum and iron phosphates may be due to two causes:

1. Dehydration of the mineral and dehydration of the aluminum and ferric hydrates associated with the phosphate.

2. Destruction of the physical structure of the minerals. The first cause seems to be the more logical one. As has been explained in experiment 1, the basic phosphates are less available than the non-basic ones. With the lazulite, wavellite, and Saldanha phosphates we have associated a quantity of aluminum hydrate. Ignition converts the hydrates into oxides:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

With dufrenite we have associated ferric hydrate which is dehydrated:

$$2Fe(OH)_3 \rightarrow Fe_2O_2 + 3H_2O$$

Now aluminum and ferric oxides are far less soluble than aluminum and ferric hydroxides, so that they would, therefore, exert a less depressing effect on the availability of the phosphates. No doubt these oxides will slowly again be converted into hydrates in the soil, but this hydration is slow and furthermore in the case of aluminum hydrate, as hydration proceeds, the lime will precipitate the aluminum as calcium aluminate.

$$2Al(OH)_3 + 3Ca(OH)_2 \rightarrow Ca_3Al_2O_6 + 6H_2O$$

This precipitation will also be more effective than when the lime has to act on the aluminum hydrate en masse. The inability of lime to remove the ferric hydrate explains the smaller effect of ignition on the availability of the dufrenite.

In the unlimed pots treated with ignited aluminum phosphate and in all the pots treated with ferric phosphate, the process of hydration of the oxides is gradual so that most of the alumina and ferric oxide will at first occur as partially hydrated oxides: $AlO(OH)$, $Al_2O(OH)_4$, $FeO(OH)$, $Fe_2O(OH)_4$, and numerous others. These partially hydrated oxides are not as soluble as the fully hydrated ones and would therefore exert less influence on the solubility of the phosphates, their hydrolysis, and final assimilation by the plants.

The destruction of physical structure of the minerals may, of course, be an important consideration. The solubility of the minerals may readily be greatly altered by destruction of the crystalline structure. The natural

solubility of the minerals will greatly affect the rate of hydrolysis of the various minerals. There are large possibilities for accounting for many riddles with regard to phosphates on the basis of crystalline structure of the minerals.

Quartaroli (63) claims the existence of two dicalcic phosphates which he represents schematically by $Ca/Ca/(HPO_4)_2$, and $\begin{matrix}Ca\\Ca\end{matrix}\Big|(HPO_4)_2$. The first is amorphous and transformable into $Ca(H_2PO_4)_2$ and the second is crystalline and not transformable into $Ca(H_2PO_4)_2$. He suggests the possibility of four forms of tricalcium phosphates which he represents schematically as:

$$(A)\ /\ Ca\ /\ Ca\ /\ Ca\ /\ (PO_4)_2$$

$$(B)\ \Big|\ Ca\ \Big|\ \begin{matrix}Ca\\Ca\end{matrix}\Big|\ (PO_4)_2$$

$$(C)\ \Big|\ Ca\ \Big|\ \begin{matrix}Ca\\Ca\end{matrix}\Big|\ (PO_4)_2$$

$$(D)\ \Big|\ \begin{matrix}Ca\\Ca\\Ca\end{matrix}\Big|\ (PO_4)_2$$

(A) would be gradually transformable into dicalcium phosphate, then monocalcium and finally into phosphoric acid; (B) would be transformable into the crystalline type of dicalcium phosphate and would not be able to produce any monocalcium phosphate; (C) would pass from tricalcium phosphate to the monocalcium phosphate without yielding the dicalcium phosphate and finally form phosphoric acid; (D) cannot be converted into di- or monocalcium phosphate but passes directly to phosphoric acid. Quartaroli has proven the presence of two lithium phosphates. He claims that phosphorites are mixtures of the four forms of calcium phosphate. Aluminum and iron phosphates would lend themselves to the production of similar isomers. Perhaps the variability inter se in availability of calcium phosphates, aluminum phosphates, and iron phosphates is due to the varying proportions of the different isomers in the several minerals. Ignition may or may not alter the proportions of the various isomers and so exert its effect on the availability of the various phosphates. The differences in the availability of lazulite, wavellite, and Saldanha phosphates, that of Florida rock and Laingsburg phosphate, etc., may easily be due to the proportions of the various possible isomers as suggested by Quartaroli.

It is very remarkable that ignited wavellite and Saldanha phosphates on the limed pots should have produced larger crops than even any of the pure phosphates. The availability of lazulite was much increased as a result of the ignition but in no form did the lazulite prove nearly as good as wavellite or Saldanha phosphates. This proves that there is a fundamental difference between the aluminum phosphates in these three minerals. Neither the crystalline structure nor the presence of aluminum hydrate can be designated

as the reason. It seems that Quartaroli has made a very notable contribution to our understanding of the phosphates we deal with in agriculture.

Plate 3, figure 2, shows the relative growth made by the buckwheat with the ignited and unignited aluminum phosphate minerals.

Experiment 5

In this experiment an attempt was made to illustrate some factors, which affect the availability of phosphates.

The first factor studied was the solubility of aluminum phosphate in an alkaline solution. The plan followed was similar to that of Kossovitsch (37) described on page 356 in the survey of literature. Three pots were planted. Inside each pot there was placed a porous pot made of bauxite. The porous pot had the same depth as the gallon pots used throughout this experiment and had a diameter of about 4 inches. This pot allowed the penetration of crystalloids in solution but effectively withstood root penetration through its walls.

In pot 1, both the inner and the outer pots were filled with sand. The outer pot received an application of lime and ferric chloride. The rest of the plant-food materials were applied in a nutrient solution containing monocalcium phosphate, potassium sulfate, and magnesium sulfate.

In pot 2, the inner pot received an application of 10 gm. of wavellite well mixed with the sand and the outer pot, an application of lime and ferric chloride. The rest of the plant nutrients were added in the form of a nutrient solution containing potassium sulfate, magnesium sulfate, and potassium carbonate.

The nutrients were all applied in the manner and amounts already described, except that one-third of the potassium sulfate was replaced by an equivalent in potassium of potassium carbonate.

In pot 3, was a duplicate of pot 2, except that the wavellite was applied in the outer pot instead of the inner pot.

Inoculated annual white sweet clover seed was sowed in the outer pots. All the pots were planted in duplicate. The nutrient solutions were applied only through the inner pot. All the water added was applied to the inner pot, so that the soil solutions reaching the plant roots all passed through the walls of the porous pot. Planting occurred on March 23, 1920, harvesting on May 27, 1920.

During the first month of the growing period, it was not thought that the plants in pot 2 would survive. On pot 1, the sweet clover grew luxuriantly. On pot 3, fairly good growth was obtained. At the end of the month the plants in pot 2 suddenly began growing, those near the porous pot first, those farther away in succession until all the plants were growing. Ten plants were finally left in each pot. The yields are given in table 18.

Enough growth was obtained on pot 2 to give confidence that the plants obtained phosphorus. Thus, phosphorus must have been dissolved by the

nutrient solution and diffused through the walls of the porous pots. In alkaline soils, then, aluminum phosphate will be dissolved by the soil solution. This fact is in accord with Storer's statement (73). Plate 4, figure 1, shows a photograph of the roots of the plants clustered around the porous pots. Chemotaxis is probably the cause for the location of the roots of the plants.

The second factor studied was the solvent effect of plant roots on various phosphates.

Thin, flat, smooth-surfaced plates of plaster of Paris were made. While the plaster was setting, phosphate was dusted onto one surface through a 200-mesh sieve and smoothed over the surface, so that the entire surface was covered with a thin uniform layer of phosphate which was also firm and smooth. All portions of the plates not covered with phosphate were carefully painted with "asphaltum" paint. With a little practice very satisfactory smooth phosphate surfaces may be produced. Such plates were made using Saldanha

TABLE 18

Yields of sweet clover

POT NUMBER	WEIGHT OF CROPS		
	First pot	Second pot	Average
	gm.	*gm.*	*gm.*
1	14.25	13.62	13.94
2	3.27	2.67	2.97
3	7.87	8.7	8.31

phosphate, wavellite and Laingsburg phosphate. Each plate was placed vertically in a pot of sand moistened with a nutrient solution containing potassium sulfate, magnesium sulfate, and ferric chloride in the proportions already described in former experiments. The sand also received an application of limestone and gypsum, the latter at the rate of 200 pounds per acre. There were two plates of each phosphate. In the one case, a sweet clover plant about 6 inches tall was placed with its roots against the phosphate surface, in the other the plant was set on the side opposite to which the phosphate was to be found. Eight weeks after planting, the plants were removed from the pots and the roots and the plates examined. Plates 4 and 5, accurately depict the effect of the plant roots on the phosphate surfaces. The roots of the plants were matted all over the surface of the phosphate, a large portion of which had been removed. The pitted appearance of the plates marked clearly the corrosive effect of the roots.

The sweet clover plants using calcium phosphate developed slightly better than the other four plants but the use of only one plant precludes the drawing of any conclusions as to the best phosphate in this form.

The plant roots could find phosphate only in very limited area. Nearly all the roots were confined to that area. The demonstration, while giving no actual proof, indicates that root contact with the insoluble phosphates is important as a factor in the assimilation of such phosphorus and that roots of sweet clover have considerable ability in rendering phosphates soluble, probably as a result of acid excretion. It was noticeable that the roots growing against the phosphate plates were considerably flattened.

GENERAL DISCUSSION

The phosphorus of the soil occurs in the form of organic compounds and minerals; the latter chiefly as aluminum, calcium, iron, and magnesium phosphates. These mineral phosphates may of course be in the form of complexes with organic matter as suggested by Peterson (51), especially if the phosphates are basic ones. Acid humic bodies and acid silicates may readily form compounds with basic phosphates. Truog (77) points out that these compounds may be "very resistant and insoluble compounds."

It is the problem of agriculturists to furnish growing crops a plentiful supply of phosphorus to be drawn from the stock in the soil. Each of the various phosphorus-containing compounds has a different degree of availability and, what is perhaps more important, demands certain special conditions for its maximum availability which vary with each type of phosphate. The ideal practice for the farmer is to obtain such conditions as will yield him the largest quantity of available phosphorus per acre. In order to prevent the deterioration of the land, this involves maintaining and generally, too, increasing the stock of phosphorus in his soil. The necessity of growing and plowing under legumes to add nitrogen to the soil involves almost invariably the use of limestone. Few legumes thrive in acid soils. Apart from the question of growing legumes it is a known fact that the organisms involved in transforming organic nitrogen into the nitrate form thrive best on calcareous media. Centuries of profitable employment of lime is proof enough of the value and the necessity of its use. Drainage, cultivation, liming, and incorporation of organic matter with the soil are essential farm practices on most of the arable soils of the world. These practices must be followed. The kind and amount of phosphorus compounds to be applied, the time and manner of application, the kind of crops grown, the use of catch crops, the employment of other fertilizers not involving phosphorus are the factors which the farmer may use in order to make the best use of the phosphorus of the soil and of insuring a good supply of phosphorus to the crops he grows.

The investigations reported in this paper have shown that plants can utilize aluminum, iron, and calcium phosphates to some extent. Certain forms of each of these phosphates are better than others; certain conditions improve, other conditions impair, the availability of these phosphates. Under all conditions, however, plants are able to obtain some phosphorus from any of the minerals used. The greater the stock of phosphorus in the soil, then the

greater the amount the plants can obtain. The greater amount of surface exposed to agencies tending to dissolve the phosphorus, and the greater amount of contact of phosphate with the plant roots are two favorable factors which would multiply the effectiveness of the extra phosphate.

Insuring the presence of a large quantity of phosphorus in the soil is the solution of the fundamental soil problem. Hopkins (29) claims that good farming practice renders 1 per cent of the phosphorus in the surface layer available every year. Twenty-three hundred pounds of phosphorus per acre would insure the availability of sufficient phosphorus to produce maximum crops of such plants as corn, oats, alfalfa, wheat, etc. If Hopkins' claim is true, the first step in the solution of the phosphorus problem of the soil would be to raise the phosphate stock of the soil to the above amount.

The choice of the type of phosphorus to add is the second problem. The experiments reported above would indicate that as an average, calcium phosphates are to be preferred. In a soil well stocked with limestone, however, aluminum phosphates may be more desirable. There is no doubt that very satisfactory results may be obtained by the use of aluminum phosphate. The price of the material would be the big factor in determining the choice of phosphates. Aluminum phosphates should never be used on acid soils unless, of course, lime is applied at the same time. In fact it would be preferable to apply lime together with the aluminum phosphate so that the two may be in intimate contact in the soil. Tricalcium phosphates are used with greater effect on acid soils. Iron phosphates have a doubtful value. If the phosphate is not basic it may be applied to advantage but the lasting effects will be much lower than that for calcium phosphates or aluminum phosphates on limed soils. In choosing phosphates to apply to soil, discretion should be used. No phosphate material should be used without a preliminary test. The low assimilability of the phosphorus in dufrenite and lazulite is a warning against indiscriminate buying of these phosphates.

Aluminum, iron, and calcium phosphates vary as to the manner in which they are rendered available in the soil. It would perhaps be a good policy to apply both aluminum and calcium phosphates to the soil so as to make full use of all the reactions which tend to place phosphorus at the disposal of plants.

Considering the time of applying phosphorus, it would be wise to apply phosphorus for the green-manuring crop especially if clover, sweet clover, rape, mustard, or some such heavy feeder on phosphorus is used. These crops will then place the phosphorus they have used at the disposal of the money crops following. This practice would be especially desirable where aluminum phosphates are used With calcium phosphates, it would perhaps be more desirable to plow the phosphate into the soil with the green-manuring crop in order to utilize to the fullest extent the acids produced during nitrification of the nitrogenous material and at the same time placing the phosphorus in intimate contact with the big source of carbonic acid production. The urea experiment reported above is further support of the results of Hopkins and

Whiting (30) regarding the effect of nitrification on the availability of phosphates.

Truog (77) makes a suggestion for a rotation of crops in Wisconsin in which he introduces white mustard and rape as catch crops, the former being planted after wheat harvest, the latter, the following year in corn at the last cultivation. The third year clover is seeded in the oats, the fourth year the field remains in clover. This suggestion is an admirable one in the direction of keeping the soil well supplied with organic matter and in using other crops to help the weak feeding *Graminae* to obtain readily available phosphorus.

Acid phosphate and soluble phosphates, in general, are usually too expensive to have a place in building up the phosphorus stock of a soil. They can be used with effect in another direction. If small top dressings of this phosphate be used, they will serve to give the young seedlings a rapid start so that they will develop a strong root system which will then function in feeding the plant in later growth stages. This practice should be used only in connection with a system in which adequate provision is made for stocking the soil with phosphorus. If not, the practice will prove to be one of the best ways of rendering a poor soil poorer.

CONCLUSIONS

1. Mineral phosphates of aluminum and iron are valuable sources of phosphorus for plants; under certain conditions they are superior to calcium phosphate, under others inferior.

2. Nitrification of urea with the consequent production of acids acts very favorably in assisting plants to obtain phosphates of aluminum, iron, and calcium for food.

3. Chemically pure phosphates of aluminum and iron are as readily available to the plants tested as is pure calcium phosphate.

4. Mineral phosphates of aluminum and iron are not as readily available as the pure phosphates of the same metals due to the fact that most of them are hydrated basic phosphates.

5. Igniting the minerals, thereby dehydrating the bases associated with the phosphates and destroying the crystalline structures of the minerals, removes the drawback against the use of mineral phosphates of aluminum and iron.

6. Aluminum phosphates, whether chemically pure or in mineral form, ignited or unignited, always display their maximum effect in a calcareous medium.

7. The effect of iron phosphates is neither enhanced nor depressed by the addition of limestone under the conditions of the experiment.

8. Under the conditions of the experiments, where chiefly neutral growing media were used, tricalcium phosphates were affected adversely by the addition of limestone.

9. An alkaline soil solution dissolves aluminum phosphate and aids the plant in obtaining its phosphorus for food.

10. Contact of the roots of plants with mineral phosphates is a very important factor in the assimilation of the phosphorus by plants for food.

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PLATE 1

Fig. 1. Buckwheat six weeks old in sand culture.

Pot number	*Treatment*	*Pot number*	*Treatment*
1201A	Lazulite	1201C	Saldanha
1202A	Lazulite and lime	1202C	Saldanha and lime
1203A	Lazulite and gypsum	1203C	Saldanha and gypsum
1204A	Lazulite, lime and gypsum	1204C	Saldanha, gypsum and lime
1301A	Dufrenite	1201B	Wavellite
1302A	Dufrenite and lime	1202B	Wavellite and lime
1303A	Dufrenite and gypsum	1203B	Wavellite and gypsum
1304A	Dufrenite, lime and gypsum	1204B	Wavellite, gypsum and lime

Fig. 2. Sweet clover six weeks old in sand cultures showing effect of lime

Pot number	*Treatment*	*Pot number*	*Treatment*
x1705	Mono calcium phosphate	x1402B	Laingsburg phosphate and lime
x1202C	Saldanah phosphate and lime	x1401B	Laingsburg phosphate alone
x1201C	Saldanah phosphate alone	x1402A	Florida Rock phosphate and lime
x1202B	Wavellite and lime	x1401A	Florida Rock phosphate alone
x1201B	Wavellite alone	x1601	Bonemeal and lime
x1302B	Vivianite and lime	x1602B	Bonemeal alone

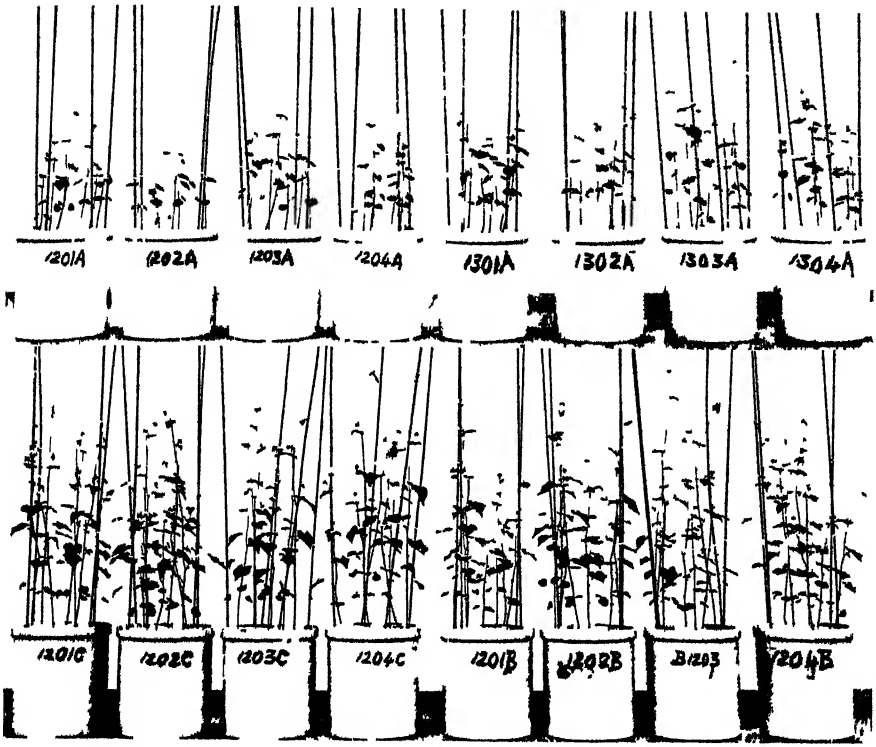

1201A
1202A
1203A
1204A
1301A
1302A
1303A
1304A
1201C
1202C
1203C
1204C
1201B
1202B
B1203
1204B

FIG. 1.

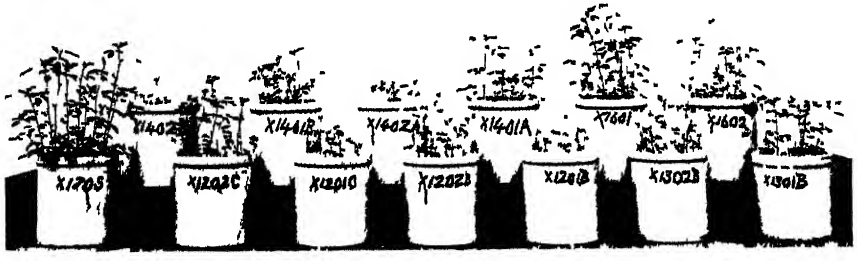

X1403
X1441B
X1402A
X1401A
X1601
X1602
X1203
X1202C
X1201C
X1202B
X1201B
X1302B
X1301B

FIG. 2.

PLATE 2

FIG. 1. Wheat on brown silt loam series showing the effect of urea on the availability of aluminum and iron phosphates.

FIG. 2. Wheat on yellow silt loam series showing the effect of urea on the availability of the calcium phosphates.

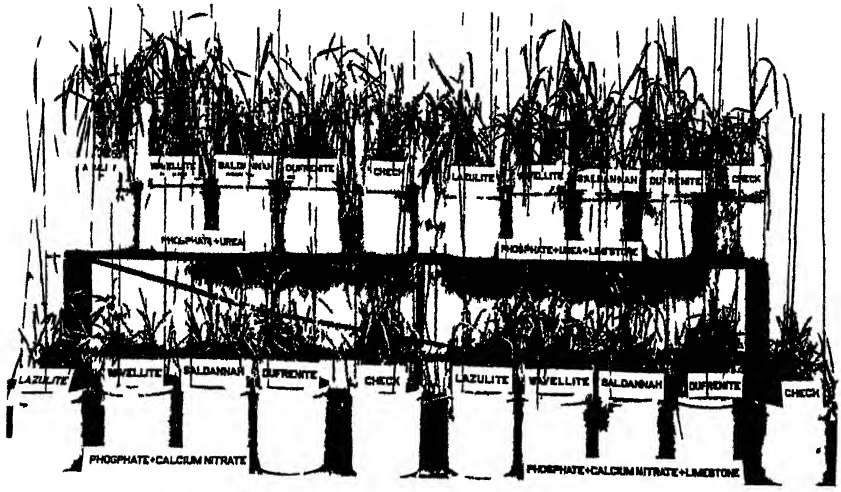

LAZULITE
WAVELLITE
BALDANNAH
DUFRENITE
CHECK
PHOSPHATE+UREA
PHOSPHATE+UREA+LIMESTONE
PHOSPHATE+CALCIUM NITRATE
PHOSPHATE+CALCIUM NITRATE+LIMESTONE

FIG. 1.

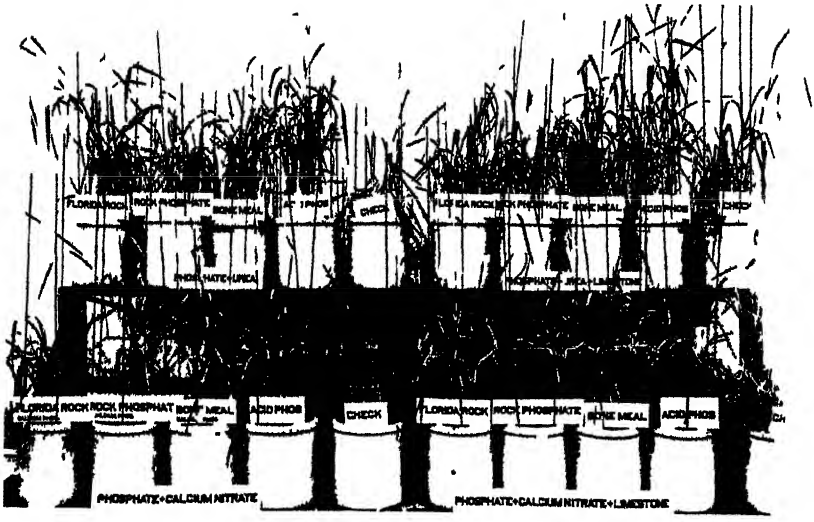
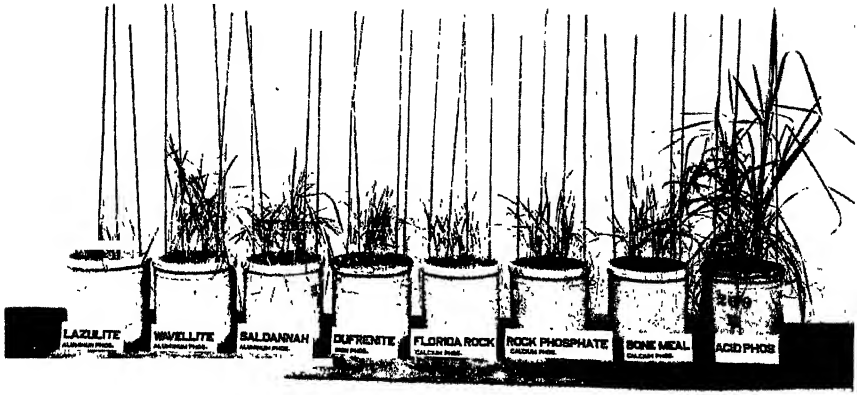

FLORIDA ROCK
ROCK PHOSPHATE
BONE MEAL
ACID PHOS
CHECK
PHOSPHATE+CALCIUM NITRATE
PHOSPHATE+CALCIUM NITRATE+LIMESTONE

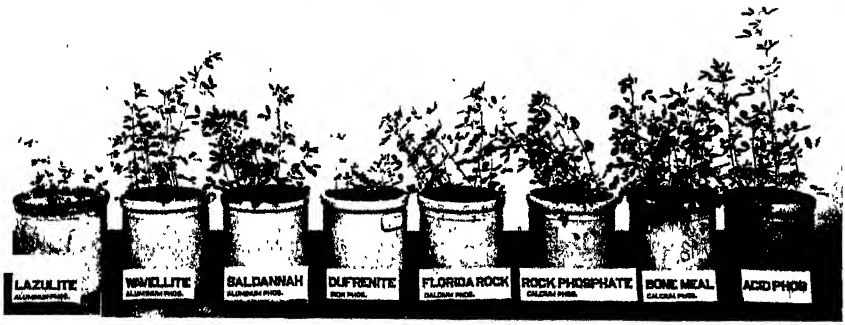
FIG. 2.

PLATE 3

FIG. 1. Wheat and clover in sand series showing the best pot with each of various phosphates.

FIG. 2. Buckwheat on sand culture showing effect of ignition on availability of aluminum phosphates.


LAZULITE
WAVELLITE
SALDANNAH
DUFRENITE
FLORIDA ROCK
ROCK PHOSPHATE
BONE MEAL
ACID PHOS


LAZULITE
WAVELLITE
SALDANNAH
DUFRENITE
FLORIDA ROCK
ROCK PHOSPHATE
BONE MEAL
ACID PHOS

LAZULITE
WAVELLITE
SALDANNAH

PLATE 4

FIG. 1. Roots of sweet clover clinging to the porous pots. Pot on right received soluble phosphorus.

FIG. 2. Effect of sweet clover roots on smooth surface of wavellite.

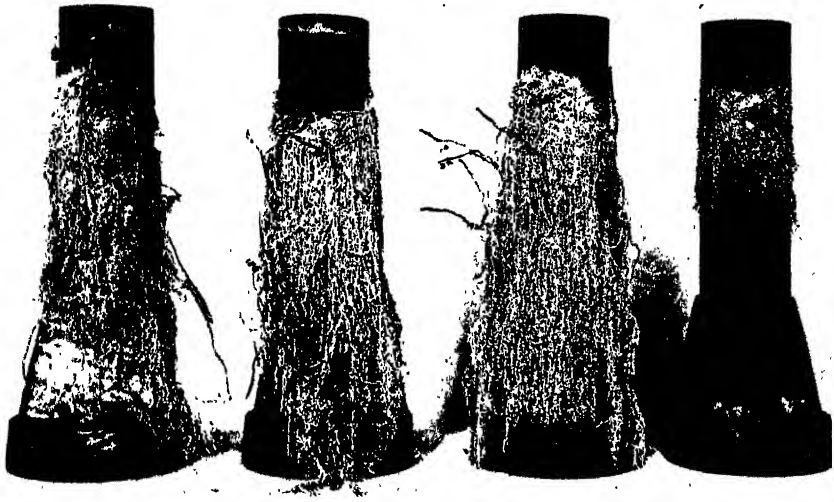


FIG. 1.

FIG. 2.

PLATE 5

FIG. 1. Effect of sweet clover on smooth surface of Laingsburg phosphate (rock phosphate).

FIG. 2. Effect of sweet clover on smooth surface of Saldanah phosphate.

FIG 1

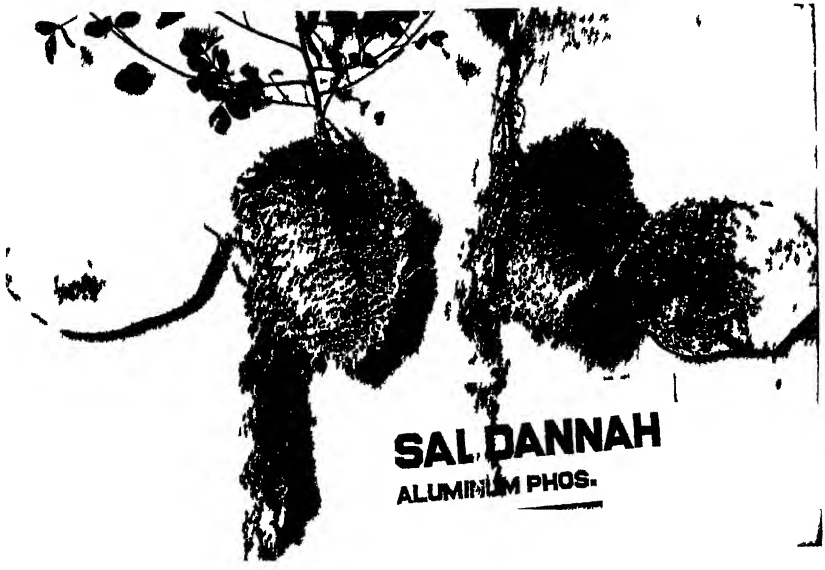


FIG. 2

PLANT INDICATORS OF SOIL TYPES[1]

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HISTORICAL

Development of the idea of plant indicators

From ancient times more observant people have associated certain plants with definite soil conditions as indicators of that condition. Thus Cato, bluff farmer-statesman, notes those growing on good wheat land while Pliny (16) records these as "dwarf elder, wild plum, rubus, plants which develop 'bulbs,' trefoil, oak, wild pear and apple." About the same time, at the opening of the Christian era, Columella (3) adds "rushes, reeds, grass, clover, and other plants known to search for water and sweetness." All of these plants do not indicate good wheat land with us but show that correlation between soil and flora was early established. Similar ideas were held throughout the Middle Ages and were transferred to the New World by those early settlers who were Classicists as well as farmers.

The scientific aspect however developed after plant physiology had its beginning, and we note among those early workers King, 1685; Degner, 1729; Buffon, 1742; and Biberg, 1749. The importance of plant indicators was suggested by Linné, 1751; emphasized by Heldenberg, 1754; while Schuow, 1832, classified them by habitats. During the nineteenth century two schools of thought arose, those who emphasized chemical influence of soil (Nageli, Contejean, Hilgard, and Schimper) and those who believed in the physical theory founded by Thurmann, 1849.

Much of the work on plant indicators has been done in this country and within the last two decades. One of our pioneer investigators was Edmund Ruffin (17) of Virginia, who contrasted the pines and andropogon of shelly lands with black locust, hackbeery, and pawpaw of rich river margins, and noted that "trees which thrive on one class are seldom found on the other, or if found, are stunted." Hilgard in his work on plant indicators stressed size, form and relative development of a plant association. Chamberlain, 1871, emphasized importance of the community as a unit in observation rather than a species. At the end of the century, 1898, Merriam summed up existing knowledge, and though his studies were based on temperature yet his efforts in bringing together facts from remote sources stimulated all branches

[1] A thesis presented to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Master of Arts. The author is indebted to Prof. John W. Harshberger for suggestion of the topic of this thesis and for his constant helpfulness.

of ecology. Hilgard, 1906, next stressed relation of plants to lime and to water while Clements, 1910, correlated certain plants with soil adapted for crops. Next year Shantz's publication demonstrated use of the quadrat method. Later, in 1917, he used plant types as indicators of soil conditions, making these a basis of classification of government lands. Weaver, 1919, noted the significance of roots as indicators.

Classification of plant indicators

After a definite relation had been established between certain plants and the soils upon which they grew, attemps were made to classify these plants. Contejean proposed relation to lime as a criterion, dividing plants into three groups: calciphile (lime-loving), calcifuge (lime-hating), and indifferent. While certain species are undoubtedly calciphile or calcifuge yet objections have been raised to this classification since a species growing upon a soil lacking in lime is not necessarily calcifugous. Thus White (24) and Pipal (15) have shown that sorrel (*Rumex acetosella*) grows on sour soil because there it has less competition; it grows luxuriantly on lime soil if not choked by other plants. The criterion was changed to relative acidity with the three classes acid-tolerant, acid-intolerant and indifferent. The objection has been made to this classification that it would seem to indicate actual destruction of plant tissues by the soil acid. Soil acids do not attack root tissues but interfere with physiological activities of metabolism.

Tolerance was naturally applied first of all to crop plants and Coville (5) has been an ardent investigator in this field. He has shown that certain plants may thrive in acid soils(sixteen species including strawberry, potato, corn and oats), while others (as alfalfa) die in an acid soil no matter how fertile. Intolerance is not a family but a species character for legumes other than alfalfa, as cowpea or hairy vetch, produce heavy growth in acid soil. Detailed studies on some species were made in their relation to hydrogen-ion concentration similar to that of Joffe (12) on alfalfa until Truog (20) was able to list sixty-two species, mostly cultivated which showed relative tolerance.

Attention had been paid to economic plants and even in the woods trees alone were taken into consideration as indicators. These, of course, indicate subsoil conditions, so that it remained for Cajander, 1909, to point out the importance of ground cover or undershrubs as indicative of soil conditions beneath. In forests of Germany he was able to work out a satisfactory classification. Later workers correlated forest types with agricultural possibilities and with the relations of water, light and fire. Korstian, 1917, noted that growth of a dominant tree is the best indicator of the quality of a forest site.

Specificity of plants to soil types

Previous work had shown that species may be associated definitely with certain kinds of soil. Even the untrained had developed the proverb that "a limestone country is a rich country." Even some apparent exceptions have been shown to be apparent only. Thus Wherry (22) in studying the walking-fern (*Camptosorus rhizophyllus*) found locaties as at Lewisburg where the plant grew on slate soil, normally acid, while the plant is a calciphile. Upon chemical examination it was found that the soil in which the roots grew was alkaline rather than acid. The walking fern is designated as specific to alkaline soil.

But comparatively little work has been done in correlation of plant forms with soil types: "a soil type is a soil which throughout the area of its occurrunce has the same texture, color, structure, character of subsoil, general topography, process of derivation and derivation from the same material" (19). Some studies have included soil types as that of Fred and Graul (7) with Colby silt loam and Plainfield sand in Wisconsin; of Bear (2) with Dekalb silt loam, West Virginia, and Wooster silt loam, Ohio; and of Gillespie and Hurst (8) on Caribou and Washburn loams in Maine. Pennell (13,14) has given an admirable study of the Conowingo Barrens of Chester county, Pa., and lists plants confined to the Barrens, noting also the

distinction between the xerophytic flora of the ridges and the more mesophytic flora of the clay regions adjoining. Sharp and Hoagland (18) tested a variety of soils with the hydrogen electrode, finding a range of pH values of 3.7 to 9.7.

OBJECT

The writer has had for his object the determination whether a general hydrogen-ion concentration, or "mode" (9), may be assigned to each of the soil types of southeastern Pennsylvania, and whether a definite relation exists between these soils and the flora growing upon them.

SOIL TYPES

The region studied is that portion of Chester County lying within a four-mile radius about Paoli; it is dominated by the Chester Valley, which is bounded on either side by low ranges of hills running northeast and southwest, and the soil areas have the same general trend. The soils are almost all upland residual and belong to that region where the Coastal plain passes into the Piedmont. There are three small areas of Pensauken formation in the Valley and some meadow is found but most of the soils are residual from Palaeozoic rocks. From north to south we meet the following belts of loam [For a more detailed description see Bascom (1)]:

1. Chester loam. This loam forms extensive tracts north and south of the Valley Hills consisting of hilly land with alternate woods and farms, the fields of which are so steep in cases as to be troubled with washing; there are numerous streams and the larger ones flow through narrow wooded valleys often of wild beauty. The surface soil is yellow brown with yellowish subsoil and contains scattered rounded boulders seen on the surface especially in pastures along streams. It is "derived from igneous and metamorphic rocks, principally from gneiss and mica schists with considerable areas from gabbro-diorite and other igneous rocks" of Pre-Cambrian age (19). Analysis of Wissahickon mica-gneiss showed the following content:

	per cent		*per cent*
SiO_2	66.13	FeO	3.19
Al_2O_3	15.11	MgO	2.42
Fe_2O_3	2.52	MnO	0.20

2. Dekalb loam. Derived from Chickies quartzite, this loam chiefly covers the North Valley Hill and in places, especially on the Valley Forge hills, becomes colluvial. Here as on Mount Joy and Mount Misery the slopes are inclined forty degrees with the horizontal and are composed of irregular slates between which are pockets of soil supporting a rather sparse growth of undershrub and scattered trees. The soil is a loam from Cambrian sediments, light, often gray, with yellow subsoil and is distinctly sandy; it is relatively high in aluminum and iron:

	per cent		*per cent*
SiO_2	56.35	CaO	0.19
Al_2O_3	23.21	Mn	trace

3. Hagerstown loam. This occupies the Chester Valley and is derived from Shenandoah limestone of Ordivician times; the soil is rich brown with yellow clay subsoil. The valley is three miles wide at its greatest width and its floor is of uneven contour, containing stretches of flat land with sinks and numerous streams which often have steep rocky banks. Most of the land is farmed and there are but few areas of woodland. Near the South Valley Hill the limestone becomes admixed with feldspar to form bastard limestone and a rather different type of soil. There also appear near this ridge several lenticular hills of micaceous schist synclinal or intercalated in the limestone. The following analysis was made of some typical valley limestone:

	per cent		*per cent*
SiO_2	24.23	$CaCo_3$	40.27
Al_2O_3	1.12	$MgCo_3$	31.24
Fe_2O_3	1.06		

4. Manor loam. Overlying the South Valley Hill this loam is residual from Octoraro schists of Ordivician time. The surface soil is yellow becoming, in contrast to most soils, dark with cultivation; it contains mica particles and small fragments of slate while the subsoil is often deep red. A typical analysis is the following:

	per cent		*per cent*
SiO_2	39.35	FeO	9.00
Al_2O_3	31.92	CaO	
Fe_2O_3	2.19	MgO	3.08

These hills are lower than the North Valley Hills and are indented by many stream-ravines. In these ravines is found a rich brown soil overlying the usual yellow subsoil, a loam differing from other portions of the Manor series not only in physical appearance but in the flora growing upon it, and the writer has therefore distinguished it as Manor Valley loam. Frequently swamps occupy these ravines and then acid rather than alkaline conditions prevail.

Upon the hills the soil becomes very thin, the slates larger and more abundant with jutting ledges of schist and quartz; this soil is called Manor stony loam.

5. Conowingo loam. South of the Valley Hills lies a long uneven descending slope in which Manor soil gives place to Chester loam. Across this portion of the Chester series runs a part of the Conowingo Barrens, represented by a few low ridges with a wide area of clay on either side. This loam is "rich in iron-magnesium silicates but almost lacking in lime, potash or other desirable constituents." In this study the clay is considered as Conowingo loam; the ridges are more acid.

METHOD

These soil types were tested for acidity by the colorimetric method. The process used at first was that described by Wherry (23). All tests were made in the field to avoid possible changes in acidity.

Modifications of the method were soon found necessary however. To assure comparable results similar quantities of material must be used; volume was used as a criterion rather than weight. Levels of 5 and 15 cc. of water were marked on the test tubes employed, soil being lightly compacted to the 5-cc. level and water being added to the 15-cc. level, the tube thoroughly shaken and then allowed to stand until the suspension had settled (often requiring considerable time).

Comparison of color produced by the color indicator with that on the chart published by Dr. Wherry did not prove satisfactory and it is hoped to continue the work with glycerophosphate buffers of a 0.2 interval.

First tests did not allow for carbon dioxide content of the soil solution. In conversation with the writer Dr. Osterhout suggested that carbon dioxide might have considerable influence on a soil test. Apparatus was prepared which could be readily carried into the field: air is passed through a NaOH tube into a vial containing a sample of the soil solution with two drops of indicator, a glass trap being interposed between the U-tube and the vial. Cotton plugs placed in the arms of the U-tube and of the trap prevent passage over of NaOH. With these precautions no change could be detected in the pH value. This result is in accord with Hoagland and Sharp (11) who state that, as a result of their experiments, "no permanent change in soil reaction could be attributed to the carbon dioxide."

Experiments were first made with topsoil which, of course, gave results indicative primarily only of soil conditions for herbs. To discover conditions in the subsoil samples were taken with which a soil auger consisted of a $1\frac{1}{2}$-inch wood auger fastened to sections of gas pipe which could be uncoupled with wrenches and carried in a case in the field. Borings with this auger may be made up to ten feet, though most of the soils were not so deep and in Manor stony loam no borings could be made, for here the loam is decidedly minor to slates and jutting ledges of rock. Care must be taken to prevent contamination of the sample as the auger is drawn out of the boring.

RESULTS

From determinations made by the colorimetric method an average reaction was derived for each soil type:

SOIL TYPE	pH VALUE
Hagerstown	7.2
Manor valley	7.2
Conowingo	7.1
Chester	7.0
Manor	6.6
Dekalb	6.2
Manor stony	5.75

These values are simply averages for the whole area covered by each loam; particular localities may have a reaction varying by a factor of $\pm\sqrt{10}$ (pH 0.5) or even more in a few cases from causes noted below.

The values given represent surface soil conditions. Some borings have been made into the subsoil with the soil auger but not enough data is accumulated to formulate conclusions as to its acidity.

TABLE 1

Plants characteristic of the soil types

TREES	SHRUBS	HERBS
Hagerstown loam		
†*Juniperus virginianum* *Quercus alba* *Ulmus americana* **Celtis occidentalis* *Lirodendron tulipifera* *Platanus occidentalis* *Negundo aceroides* *Fraxinus americana*	*Corylus americana* *Celastrus scandens* *Staphylea trifolia*	**Pellaea atropurpurea* **Camptosorus rhizophyllus* *Equisetum hyemale* *Asarum canadensis* *Aquilegia canadensis* *Dicentra cucullara* *Mitella diphylla*
Manor valley loan		
Ostrya virginiana *Lirodendron tulipifera* *Prunus pennsylvanica* **Fraxinus pennsylvanica* var. *lanceolata* (in swamps)	*Benzoin aestivale* *Hamamelis virginiana* *Vaccinium corymbosum*	*Osmunda cinnamomea* *Lycopodium annotinum* *Erythronium americanum* *Medeola virginiana* *Euonymus obovatus* *Viola scabriuscula* *Panax trifolium* **Trientalis americana* *Collinsonia canadensis* *Aster divaricatus*
Conowingo loam		
Juniperus virginianum **Quercus stellata* *Acer rubrum*	*Smilax rotundifolia*	*Andropogon scoparius* **Paspalum pubescens* **Cerastium oblongifolium* *Viola fimbriatula* **Aster depauperatus*
Chester loam		
Carya ovata *Quercus rubra* *Q. coccinea* *Q. velutina* *Ulmus americana* *Prunus americana* *Cornus florida* *Fraxinus americana*	*Amalenchier canadensis* *Rhus glabra*	*Lillum superbum* *Smilax herbacea* *Iris versicolor* *Houstonia cerulea* *Specularia perfoliata* *Solidago rugosa*

TABLE 1—*Concluded*

TREES	SHRUBS	HERBS
	Manor loam	
Carya alba	*Rhus copallina*	*Pteris aquilina*
C. cordiformis	*Viburnum acerifolium*	*Andropogon scoparius*
Betula lenta		**Gillenia trifolia*
Castanea dentata		*Viola pubescens*
Sassafras variifolium		**Solidago polycephala*
Robinia pseudo-Accaia		*Aster ericoides*
	Dekalb loam	
Carya ovata	*Smilax rotundifolia*	*Iris versicolor*
C. alba	*Amelanchier oblongifolia*	*Cassia marilandica*
Quercus nana	*Rhodendron nudiflora*	*Viola fimbriatula*
**Q. ilicifolia*	*Vaccinum corymbosum*	*Veronica officinale*
	Symphorocarpus vulgaris	*Solidago pubescens*
	Manor stony loam	
Castanea dentata	*Kalmia latifolia*	*Polypodium vulgare*
**Quercus prinus*	*Gaylussacia baccata*	*Andropogon glomeratus*
	Rhododendron nudiflora	*Cassia nyctitans*
		Epigea repens
		Seriocarpus asteroides

* Species marked by an asterisk are almost entirely confined to soil type.

† Plants in both tables are arranged according to the classification in the seventh edition of Gray's Manual.

During the winter it was found that falling snow is neutral in reaction and continues neutral for several days or as long as it remains in the open country. In proximity to steam railroads, however, snow became covered with fine cinders in a few hours and the reaction changed from neutral to a pH value of 4.5 or 4. Since this cover of cinders is quite uniform and extends for about a mile on either side of the railroad, depending upon the wind, the acidity of these regions would probably be affected.

Contrast of winter with summer conditions has been studied but not enough tests have been made to establish definite conclusions. Those made indicate a higher degree of acidity in late summer, especially in such types as the Conowingo. This would be expected since these types have either a thin layer of loam on bedrock or too great a subsoil drainage; the flora is sparser and less moisture is conserved. Vegetable decay is then halted and a more acid leaf mold results.

The relation of these results to the flora growing upon the different loams is shown in the accompanying tables. It will be seen from table 1 that certain plants are characteristic of each of the different soil types, and that species of the same family may be characteristic of widely different types of soil.

TABLE 2

Plants found on the different soil types

NAME OF PLANT	HAGERSTOWN	MANOR VALLEY	COWOWINGO	CHESTER	MANOR	DEKALB	MANOR STONY
Pteridophyta							
Polypodium vulgare L.	−*	−	−	+	−	+	+
Pteris aquilina L.	−	−	+	+	+	+	−
Pellaea atropurpurea Link	+	−	−	−	−	−	−
Asplenium platyneuron (L) Oakes	+	+	+	+	+	+	−
Camptosorus rhizophyllus Link	+	−	−	−	−	−	−
Polystichum acrostichoides Schott	+	+	(+)	+	+	+	−
Aspidium marginale Sw.	+	+	(+)	+	+	+	−
Onoclea sensiblis L.	+	+	+	+	+	+	−
O. cinnamonea L.	−	+	(+)	+	−	+	−
Botrichium virginianum Sw.	+	+	+	+	+	+	−
Equisetum arvense L.	+	+	−	−	+	−	−
E. hyemale L.	+	−	−	−	−	−	−
Lycopodium complanatum L.	−	−	−	−	(+)	+	−
L. annotinum L.	−	+	−	+	(+)	+	−
var. *flabelliforme* Fernald	−	−	−	+	+	+	−
Spermatophyta							
Juniperus virginianum L.	+	(+)	+	+	+	+	(+)
Tsuga canadensis L.	−	−	−	−	−	+	+
Andropogon glomeratus BSP.	−	−	−	−	(+)	−	+
Andropogon scoparius L.	−	−	+	−	+	+	−
Arisaema triphyllum Schott	+	+	−	+	+	(+)	−
Veratrum viride Ait.	−	+	−	(+)	−	(+)	−
Uvularia perfoliata L.	−	+	−	+	+	+	−
Lillium superbum L.	−	−	−	!	−	−	−
L. canadensis L.	−	−	−	!	−	+	−
Smilacinia racemosa (L.) Desf.	+	+	−	+	+	+	−
Maianthemum canadense Desf.	+	+	(+)	+	+	(+)	−
Medola virginiana L.	+	+	−	+	−	(+)	−
Smilax herbacea L.	+	+	−	+	+	+	−
S. rotundifolia L.	−	−	!	+	+	+	−
Iris versicolor L.	−	−	−	+	−	+	−
Cypripedeum acaule Ait.	−	−	−	−	+	+	−
Julans cinerea L.	+	+	−	−	+	−	−
J. nigra L.	!	+	(+)	+	+	+	−
Carya ovata (Mill) K. Koch	−	−	−	+	−	+	−
C. alba (L) K. Koch	+	+	−	−	+	+	−
C. glabra (Mill) Spach	+	+	−	−	+	+	+
C. cordiformis (Wang) K. Koch	+	+	+	−	−	−	−
Corylus americana Walt.	+	−	−	+	−	+	−

* Explanation of symbols: + Present; − Absent; ! Marked abundance; (+) Secondary.

TABLE 2—*Continued*

NAME OF PLANT	HAGERSTOWN	MANOR VALLEY	CONOWINGO	CHESTER	MANOR	DEKALB	MANOR STONY
Ostrya virginiana (Mill) K. Koch	−	+	(+)	−	−	−	−
Betula lenta L.	−	−	−	−	+	+	(+)
Alnus rugosa (DuRoi) Spreng.	(+)	+	(+)	+	+	+	−
Fagus grandifolia Ehrh.	+	+	(+)	+	+	+	(+)
Castanea dentata Borkh.	−	−	(+)	+	+	+	!
Quercus alba L.	+	+	(+)	+	+	+	−
Q. stellata Wang.	−	−	+	−	−	+	−
Q. prinus L.	−	(+)	−	−	−	+	!
Quercus rubra L.	+	+	−	+	+	−	−
Q. palustris Muench.	−	−	−	+	−	−	−
Q. coccinea Muench.	+	−	+	+	+	+	(+)
Q. velutina Lam.	+	+	+	+	+	+	+
Q. ilicifolia Wang.	−	−	+	−	−	+	−
Ulmus fulva Michx.	+	+	−	+	(+)	−	−
U. americana L.	+	+	−	−	+	−	−
U. racemosa Thomas	−	−	−	−	+	−	−
Celtis occidentalis L.	!	−	−	−	(+)	−	−
Broussonetia papyrifera (L) Vent.	+	+	−	+	−	−	−
Asarum canadense L.	+	−	−	−	−	−	−
Cerastium oblongifolium Torr.	−	−	!	−	−	−	−
Claytonia virginica L.	+	+	−	+	+	+	−
Anemonella thalictroides Spach.	+	+	−	+	+	(+)	−
Anemone riparia Fernald	−	+	−	+	−	(+)	−
Hepatica triloba Chaix.	+	(+)	−	+	+	+	−
Aqilegia canadensis L.	!	−	−	−	−	−	−
Lirodendron tulipifera L.	!	+	−	+	+	+	−
Podophyllum peltatum L.	+	+	−	+	+	(+)	−
Sassafras variifolium (Salis.) Fize	+	+	(+)	+	+	+	(+)
Benzoin aestivale (L) Nees.	+	+	(+)	+	+	+	−
Sanguinaria canadensis L.	+	+	−	+	+	(+)	−
Cheilodonium majus L.	!	(+)	−	−	+	−	−
Dicentra cucullara (L) Bernh.	+	−	−	+	−	−	−
Dentaria diphylla Michx.	+	+	−	+	−	−	−
Sedum telephoides Michx.	−	−	−	−	−	+	−
Saxifraga virginensis Michx.	+	−	+	+	+	+	−
Heuchera americana L.	+	−	(+)	+	+	+	−
Mitella diphylla L.	+	−	−	−	−	−	−
Hamamelis virginiana L.	+	+	−	+	(+)	+	−
Platanus occidentalis L.	!	−	−	+	+	−	−
Gillenia trifolia (L) Moench.	−	−	−	−	+	−	−
Amelanchier canadensis L.	−	+	−	+	+	!	−
A. oblongifolia Roem.	−	−	−	−	−	+	−
Prunus virginiana L.	+	+	(+)	+	+	+	(+)

TABLE 2—*Continued*

NAME OF PLANT	HAGERSTOWN	MANOR VALLEY	CONOWINGO	CHESTER	MANOR	DEKALB	MANOR STONY
P. pennsylvanica L.	+	+	(+)	+	+	+	−
P. americana Marsh.	−	−	(+)	+	+	+	−
Gleditsia tricanthos L.	+	−	−	−	−	+	−
Cassia marilandica L.	+	−	−	+	−	+	−
C. nyctitans L.	−	−	−	−	(+)	−	+
Baptisia tinctoria (L) R. Br.	−	−	(+)	−	−	+	+
Robinia pseudo-Accacia L.	+	(+)	−	+	!	+	−
Geranium maculatum L.	+	+	−	+	+	+	−
Ailanthus glandulosa Desf.	+	+	−	+	+	+	(+)
Rhus typhina L.	−	+	−	+	+	+	−
R. glabra L.	+	+	(+)	+	+	+	−
R. copallina L.	−	−	−	−	+	+	−
R. toxicodendron L.	+	+	+	+	+	+	+
Euonymus americanus L.	−	−	−	−	+	−	−
E. obovatus Nutt.	−	+	−	−	(+)	−	−
Celastrus scandens L.	+	−	−	−	+	−	−
Staphylea trifolia L.	+	−	−	−	−	−	−
Acer rubrum L.	+	+	+	+	+	+	(+)
A. Negundo L.	+	−	−	+	+	−	−
Psedra quinquefolia (L) Greene	+	+	+	+	+	+	−
Vitis cordifolia Michx.	+	+	−	+	+	+	−
Hypericium gentianoides (L) BSP.	−	−	−	−	−	+	+
Viola fimbriatula Sm.	−	−	+	−	(+)	+	−
V. pubescens Ait.	(+)	−	−	−	−	(+)	+
V. scabriuscula Schwein.	+	+	−	+	+	−	−
Aralia nudicaulis L.	−	−	−	−	+	+	−
Osmorhiza longistylis DC.	+	+	−	+	+	−	−
Cornus florida L.	+	+	(+)	+	+	+	(+)
Nyssa sylvatica Marsh.	+	+	(+)	+	(+)	+	−
Chimaphila maculata (L) Pursh.	−	−	−	+	+	+	−
Pyrola americana Sweet	−	+	(+)	−	−	+	−
Kalmia latifolia L.	−	−	−	−	(+)	+	−
K. angustifolia L.	−	−	−	−	−	+	−
Epigea repens L.	−	−	−	+	+	+	!
Rhododendron nudiflorum Torr.	−	(+)	(+)	+	!	!	(+)
Gaylussacia baccata C. Koch	−	−	−	(+)	+	+	+
Vaccinium corymbosum L.	−	(+)	(+)	+	+	+	−
Lysimachia quadrifolia L.	−	−	−	+	+	+	(+)
Trientalis americana Pursh.	−	(+)	−	−	−	−	−
Fraxinus americana L.	+	+	−	+	+	+	−
F. pennsylvanica Marsh.	+	+	−	−	+	−	−
var. *lanceolata* (Borkh) Sarg.	−	(+)	−	−	−	−	−
F. nigra Marsh.	+	−	−	+	+	−	−

TABLE 2—*Concluded*

NAME OF PLANT	HAGERSTOWN	MANOR VALLEY	CONOWINGO	CHESTER	MANOR	DEKALB	MANOR STONY
Asclepias tuberosa L.	−	−	−	−	+	÷	−
Phlox sublata L.	−	−	+	−	−	−	−
Monarda fistulosa L.	+	−	−	−	+	−	−
Pycnanthemum torrei Benth.	+	−	(+)	−	+	+	−
Cunila originoides (L) Britton	−	−	−	−	+	+	−
Collinsonia canadensis L.	+	!	−	+	−	(+)	−
Paulownia tomentosa (Thunb) Steud.	+	+	−	−	−	−	−
Veronica officinalis L.	+	−	+	+	+	+	(+)
Melampyrum lineare Lam.	−	−	−	−	+	+	(+)
Plantago virginica L.	+	−	−	+	+	!	−
Mitchella repens L.	−	+	(+)	+	+	(+)	−
Symphorocarpus vulgaris Michx.	+	−	−	−	−	!	−
Viburnum acerifolium L.	+	+	−	+	+	+	−
Sambucus canadensis L.	+	+	−	+	(+)	+	−
Specularia perfoliata (L) DC	+	−	−	+	−	+	−
Campanula rotundifolia L.	+	−	−	−	+	−	−
Lobelia cardinalis L.	−	−	−	+	−	+	−
L. Kalmii	+	(+)	−	+	+	+	−
Solidago caesia L.	+	+	(+)	+	!	+	(+)
S. bicolor L.	+	(+)	(+)	+	+	+	+
S. puberula Nutt.	+	−	+	+	+	+	+
S. altissima L.	+	−	(+)	+	+	+	−
S. polycephala Fernald	−	−	+	−	+	−	−
Aster divaricatus L.	−	+	−	+	(+)	+	−
A. cordifolius L.	+	+	−	+	+	+	−
A. ericoides L.	−	−	+	+	!	+	(+)
A. depauperatus Fernald	−	−	!	−	−	−	−
A. multiflorus Ait.	+	+	+	+	+	+	−
A. dumosus L.	+	+	(+)	+	+	−	−
Seriocarpus asteroides (L) BSP	−	−	(+)	−	(+)	+	!

Compare the oaks: White oak (*Quercus alba*) is typical of rich neutral soil such as Hagerstown and Chester loams so that their abundant presence at once gives an index of soil conditions at that place. Post oak (*Quercus stellata*) is characteristic of the Barrens which, though neutral are poor because of the high magnesium content. Chestnut oak (*Quercus prinus*) is the dominant tree of acid soil, the Manor stony loam of the hills, where it is stunted by strong winds, or swampy acid portions of ravines where it can grow to large size.

Much has been written on the causes of soil acidity and many influences affecting it have been noted, soil physicists recognizing the effect of free mineral, or organic acids, colloidal material, absorption and adsorption phenomena. Effect of arrested leaf decay has been shown clearly by Coville (6) to give an alkaline soil when well-rotted but an acid soil when partially

decayed. Other factors influencing soil acidity depend upon physiographic features. Each soil type exhibits a general average acidity but the actual pH value varies with every variation of slope exposure, as has been well shown by Harshberger (10) at Guelph, Pa. Similar relations hold good in most of the ravines of the South Valley Hills where exposed dry slopes have a partially decayed leaf litter and a chestnut oak-ericaceous flora while the less exposed slopes have a well-rotted topsoil and a mesophytic flora. Degree of slope is likewise important. An admirable illustration was found among the Valley Forge Hills where Mt. Joy exhibited on the west face a gradual decrease in pH value from 7 to 5.5 in ascent with a change from a mesophytic flora to a sparse ericoid type. Relative elevation also plays a part. Depression of an area of a neutral soil type below level of ground water results in an acid soil. Examples of this were especially marked in the serpentine belt south of Paoli, where post oak and cedar gave place to chestnut and Vaccineae in swampy areas.

The physiological effect of soil acid on a plant is two fold as noted by Truog (21), indirect, as through fertility, and direct, as affecting availability of calcium.

It is suggested that the foregoing influences may aid in the development of plant varieties, and that some plants now listed as distinct may have gained their distinctive structure because of them. Thus *Viola scabriuscula* grows in rich damp neutral soil while *V. pubescens* grows in dry exposed acid soil, but on ascending an exposed hill-slope one finds intergradations of varying degrees of pubescence and of intermediate habit. However, on the lenticular knolls in the Valley where slate and limestone are interbedded *V. scabriuscula* was found growing high on the slope in pockets of limestone soil.

SUMMARY

From classic times it has been known that certain plants are indicative of conditions of the soil in which they grow. Many of the relations existing between soil and flora have been discovered but comparatively little work has been done in correlating plants with soil types. Some of these relations were investigated by the writer and a preliminary report is here given.

In soil testing the colorimetric method was used as being the most practical for field tests. Carbon dioxide of the soil solution was not found to affect the pH value in the tests.

The acidity of a soil type is a variable quantity but an average pH value may be assigned to each type. Those given represent surface conditions; borings are being made to determine subsoil acidity. Soil acid is governed in part by such factors as arrested leaf decay, and physiographic features of slope, degree of slope and relative elevation. Some types of soil seem to have an higher degree of acidity in late summer.

Soil acidity influences flora to such an extent that certain plants may be assigned as indicators, a number being listed for each type. Soil acidity perhaps induces variation in plant species.

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THE LATERITE SOILS OF FORMOSA ISLAND

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INTRODUCTION

There are in Formosa three kinds of rock which, after disintegration, form red colored soils. These are basalt, andesite and sedimentary rocks. Among these, the last mentioned is the most common as a mother rock of red soils. The soils belonging to this class occupy about 14 per cent of Formosa's cultivated area, *i.e.*, 265,000 acres. This area is located principally in the northern part of the island, and diminishes gradually toward the south except at the southern extremity. It occurs as more or less elevated land or terraces. The red colored soil always covers gravel layers which sometimes extend to a depth of several hundred feet. The gravels are roundish in shape and the red colored soil fills in between them. The soil and gravel seem to be of the same origin from a geological standpoint. Many gravels are red in color, as well as the soil surrounding them, and are, no doubt, derived from sandstones and shales. It seems, therefore, that the red colored soil is derived from the Tertiary sandstones and shales. Furthermore it is from diluvial and not from aeolian or volcanic formation, as suggested by some geologists who have visited the island. The characterisitc color of this soil is deep brick-red or brown, the color being darkened when it is moistened. Its texture is that of very heavy clay and it forms easily in lumps. When a field drys up after a rain, it becomes so hard that plowing is impossible.

The native people who live on the plateaus use this soil as a clarifying medium for their home supply of water. There are no streams and it is very difficult to get well water, hence contaminated and turbid water must be sufficiently purified for home use. To accomplish this they mix the contaminated water of a pond with soil in a barrel, stir it up and allow it to settle. In a few hours the water settles clear enough for home use. It stands to reason that colloidal substances in the soil withdraw suspended materials even including undesirable microörganisms. Stirring aids aggregation and flocculation of colloidal materials under certain circumstances.

Oxides, hydrates and some silicates of iron and aluminum represent the colloidal materials in the soil. These are found adhering to each other or coated on quartz sands. Ordinarily the alkali and alkali earth content is very low, on

account of leaching out by long weathering. Quartz, however, remains in large proportion in the soil. Humus and other organic substances are present in small quantity, since climatic conditions rarely permit their accumulation. This soil (1, 2, 3) together with two other red colored soils may in a broad sense be classified as "laterite." Originally the name laterite was applied to a red residual soil which was found in India. But the laterite is defined as a vesicular, highly ferruginous, brick-red clay soil occurring in the tropical and subtropical regions. It is derived from various rocks which are extremely disintegrated by weathering actions. The laterites in Formosa conform to this definition in that they possess such characteristics and mode of formation. A large part of the Oolong tea gardens and thousands of acres of rice fields occupy the laterite area of the Tertiary origin. Investigation looking to the improvement of fertility in the laterite soils is of greatest importance, inasmuch as its low productivity is a serious handicap in the Formosan agriculture.

Productivity of crops

The most important laterite in Formosa is a residual clay soil which originated from sandstones and shales. Consequently soluble ingredients in it have been leached out by continuous weathering actions. Various agencies of decomposition under the tropical conditions do not permit the accumulation of organic matter in the soil. On this account, chemical and physical properties of the soil are unfavorable to production of most crops. Brief note of the productivity with respect to certain crops may be of interest in connection with the laterite soil.

Tea

Among crops, the tea plant, a perennial shrub, is the most adaptable and common in the laterite area. Remarkable Oolong tea of good quality is produced on this soil. But an average production of dried tea leaves per annum is about 300 pounds per acre, which is 60 per cent of a good average tea yield.

Rice

At the foot of hills or in lower places of the laterite region which are irrigable, rice fields are quite extensive. The soil texture is very heavy and the subsoil quite impervious, therefore percolation of water through the soil is very difficult. As a result some plots are irrigated only with the natural rainfall. The general fertility is very poor and production of rice corresponds to about 50 per cent of a normal crop.

Sugar cane

Lands not suitable for tea plantation and not in the irrigable parts of this soil are used for cultivation of sugar cane, sweet potato, sesame, peanut, etc. For the production of sugar cane these lands are hardly successful on account of the difficulty with which the plant roots penetrate the soil. The cane yield therefore is ordinarily about one-third of that expected in favorable regions.

It may be said of other crops that, in general, yields are from 35 to 60 per cent of the normal. No crops grow as luxuriantly in the laterite soil as on other fertile lands. Farmers who cultivate these areas at all find it necessary to pay special attention to soil management and maintenance of its fertility.

CHEMICAL COMPOSITION

Many samples of laterite which are derived from the Tertiary rocks have been analyzed in the Government Soil Survey of Formosa. Table 1 gives the composition of five representative soils from different parts of the island.

TABLE 1

Chemical composition of five Formosan laterites

CONSTITUENTS	YOBAIREKI	SONAMPI	TAISHO NANTO	MT. TAKAO	ROPII
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Alumina, Al_2O_3	15.89	9.74	11.24	24.55	11.91
Ferric oxide, Fe_2O_3	4 36	3.46	3.85	8.39	6.83
*Ferrous oxide, FeO	1.76	1.44	1.47	2.13	2.25
Manganese oxide, Mn_3O_4	0.16	0.19	0.30	0.26	0.21
Lime, CaO	0.16	0.11	0.17	0.51	0.31
Magnesia, MgO	0.30	0.25	0.32	0.47	0.38
Potassium oxide, K_2O	0.29	0.19	0.17	0.41	0.19
Sodium oxide, Na_2O	0.27	0.84	0.33	0.61	0.20
Silica, SiO_2	71 48	72.67	76.80	57.99	73.59
Phosphorus pentoxide, P_2O_5	0.09	0.07	0.13	0.44	0.19
Sulfur trioxide, SO_3	0.03	0.09	0.09	0.34	0.20
Chlorine, Cl	0.01	0.002	0.01	0.002	0.005
Loss on ignition	6.34	10.85	4.83	6.08	4.03
Total	101.14	99.902	99.71	102.182	100.495
Nitrogen	0.12	0.06	0.12	0.16	0.14

*Includes titanium oxide, TiO_2.

It is noticeable that these soils show a composition quite different from Indian laterite (2), especially in that they contain a large amount of silica and relatively low quantity of alumina and iron oxide. The quantity of alkalies and alkaline earths in the Formosan laterite is particularly small and this is true also of the acidic elements such as phosphorous and sulfur. These facts all indicate that the soil is a residual product of rocks which were disin-

tegrated by the tropical conditions. It is recognized that no one is able to estimate exactly the degree of soil fertility by the results of chemical analyses. Such results, however, will very often aid in directing one's judgement regarding fertility. Table 1 shows that the soils mentioned are very low in plant nutrients with the exception of no. 4, the laterite of Mt. Takao. The deficiency is especially marked in the phosphoric acid and nitrogen contents of the soils described. It is supposed that aluminum and iron occur in the form of oxides, hydrates and silicates and that these elements function principally through their colloidal nature.

SEPARATION OF COLLOIDAL MATERIALS AND THEIR CHEMICAL COMPOSITION (4)

A certain amount of laterite was treated with a large quantity of distilled water, strongly agitated, and the colloidal solution separated by a Sharples centrifuge. The centrifuge bowl running at a speed of 40,000 revolutions per minute served to separate the colloidal solution from the larger soil grains. The colloidal solution was then filtered through Pasteur-Chamberland filters and the colloidal substances remaining on the filters collected for study. The colloidal solution which is characterized by its marked Brownian movement observed under the ultra-microscope, was dried and its chemical composition determined for comparison with the soil from which it was derived.

TABLE 2

Chemical composition of colloidal materials in the laterite in comparison with the original soil

CONSTITUENTS	COLLOIDAL MATERIALS	ORIGINAL SOIL
	per cent	*per cent*
Alumina, Al_2O_3	31 19	12.79
Iron oxide, Fe_2O_3	13.77	4.94
Titanium oxide, TiO_2	0.70	1.25
Manganese oxide, Mn_3O_4	0.10	0.05
Lime, CaO	0.25	0.21
Magnesia, MgO	0.99	0.38
Potassium oxide, K_2O	0.17	0.11
Sodium oxide, Na_2O	0.16	0.11
Silica, SiO_2	35.79	73.50
Phosphorus pentoxide, P_2O_5	0 41	0.24
Sulfur trioxide, SO_3	0.31	0.17
Loss on ignition	15.54	6.31
Total	99.38	100.06
Nitrogen	0.18	0.12

It is not to be doubted that colloidal substances of this soil consist mainly of aluminum and iron compounds which are assumed to be oxides, hydrates and silicates. The large amount of loss on ignition in colloidal substances sup-

ports an assumption of the presence of hydrates and hydrous silicates. Decrease of silica in the colloid indicates that the majority of quartz grains was transmitted to the solid portion. Titanium compounds were lower in the colloid, perhaps on account of their stability against disintegration.

PETROGRAPHIC EXAMINATION (5, 6)

This soil obviously contains traces of various soluble salts which, however, are not detectable unless concentrated. A preliminary petrographic examination was carried on with insoluble soil particles. For an easier observation a small quantity of the soil was washed with distilled water and the soluble as well as colloidal materials permitted to run off. The residual dried sandy portion was identified under a petrographic microscope by the standard methods. An examination showed the following minerals present:

Quartz, SiO_2
Amorphous silica, SiO_2
Hematite, Fe_2O_3
Magnetite, Fe_3O_4
Tourmaline, boro-silicate of Al, Fe, and alkali metals
Zircon, $ZrSiO_4$
Chlorite, a silicate of iron, aluminum and magnesium
Bauxite, $AlFe(OH)_3$
Hornblende, silicates of Al, Fe, Mg, Ca, Na

Among the minerals, quartz grains are the most abundant. Amorphous silica, hematite, magnetite and tourmaline in lesser quantity comprise the principal mineral ingredients of the soil. Zircon frequently comes into the optical field, but other minerals are very rare. There are, however, perhaps traces of several minerals which escaped identification. The detection of certain mineral grains serves further to confirm our judgement of the fertility of a soil.

RELATION BETWEEN COLOR OF LATERITE AND ITS IRON CONTENT

Laterite is characterized by its deep red color, owing to high iron content. In fact the name laterite originates from a Latin word, *later* which means brick. The color of Formosan laterites ranges from yellow or brown to red or deep-brown red. A series of laterite samples which have different colors from light to dark, were analyzed and compared as to the amount of iron present. Results of the analyses are given in table 3.

As is shown in table 3, the color of soils is not dependent to any considerable degree upon the iron content. It depends rather upon the degree of oxidation and distribution of iron compounds over soil grains. The finer distribution of the oxide usually indicates the deeper color, because much of ferruginous compounds form coatings on soil grains.

TABLE 3

Relation between color of laterite and its iron content

LOCATION	SOIL	COLOR	IRON OXIDE
			per cent
Boko Islets	Basaltic laterite	Brownish red	20.70
	Basaltic laterite	Deep brown	19.99
	Basaltic laterite	Reddish brown	12.08
Taichu	Tertiary laterite	Brown	3.33
	Tertiary laterite	Light brown	2.08
Boko Islets	Basaltic clay soil	Light brown	18.52
	Basaltic clay soil	Dark grey	15.02
Nanto	Tertiary loam	Grey	2.59
Mt. Ari	Tertiary clay soil	Yellow	8.00

SUMMARY

1. There is a kind of laterite which is derived from the Tertiary rocks in Formosa. It is not the same as Indian laterite, but belongs to the laterite class in a broad sense.

2. This soil covers the diluvial formation in the island and usually forms hills or plateaus.

3. It contains oxides, hydrates and silicates of aluminum and iron. These have their principal function by virtue of their colloidal nature in the soil.

4. The fertility of this soil is very poor, especially in nitrogenous and phosphatic nutrients.

5. By detection under a petrographic microscope quartz, amorphous silica, hematite, magnetite, tourmaline, zircon, etc., were identified.

6. The characteristic deep red color of this soil depends in general upon the iron oxide content and particularly upon the distribution of this upon the soil grains.

This paper is a brief note on investigation of Formosan laterite. There are many other data already available and under investigation. These will be reported in later papers.

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FURTHER STUDIES ON THE SOLUBLE SALT CONTENT OF FIELD SOILS

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In a previous publication (1) data from a limited study of the soluble salt content of soils in the field were presented and the following observations made.

1. When soils were maintained free from vegetation there was a continual variation of the soluble salt content of the stratum ¼ to 6 inch. Early in the spring the concentration was quite low but increased to a maximum in the summer and then decreased again.
2. While there were slight variations of the salt content of the subsoil 6 to 12-inch section, there was no tendency to reach a maximum and recede.
3. When no vegetation was present a considerable concentration of salts was noted in the surface ¼-inch of soil during periods of drought.
4. When the soil supported a growth of vegetation the tendency for the salts to accumulate at the surface was largely prevented.
5. Crop growth tended to decrease the amount of soluble material in the ¼ to 6 inch section and to a less extent in the 6 to 12-inch section. The nature of the crop seemed to have some bearing on this action.

These field studies have been continued and the scope of the experiments enlarged to include several other phases of the problem. The purpose of this publication is to present the data obtained during the years 1919 and 1920.

COLLECTION OF SAMPLES

In collecting the samples during 1919 three depths were considered. The surface soil to a depth of approximately ¼ inch was scraped off with a spatula. The next sample was taken to a depth of 6 inches and was called the ¼ to 6 inch section. The third sample represented the 6 to 12-inch stratum. Every precaution was taken to prevent the contamination of any sample by soil from another section. The samples were taken immediately to the laboratory, air dried and passed through a two millimeter screen. Samples were collected every month from March to Ocotber, inclusive, from areas maintained free of vegetation by scraping with a hoe and adjacent areas bearing sod or growing crops.

[1] The writer desires to express his gratitude to Dr. M. M. McCool for many valuable suggestions during the progress of this work.

METHOD OF PROCEDURE

The concentration of the soil solution was measured by means of the Beckmann thermometer. The samples were prepared by adding sufficient water to a 20-gm. sample in a freezing tube to thoroughly saturate the soil and upon standing form a column approximately 1/16 inch deep on the surface. The proper amount of water for each soil was carefully determined at the beginning of the experiment and the same amount used in each succeeding determination on the samples. It was believed that by this procedure more accurate measurements of small variations could be obtained than by the common method of adding a uniform volume of water to each soil regardless of texture. The data presented represent the average of two or more closely agreeing determinations.

EXPERIMENTAL

The data from the plots maintained free of vegetation will be considered first. The concentration of the soil solution of the $\frac{1}{4}$ to 6 inch section, as represented by the freezing point depression, for the year 1919 are given in table 1.

These data show that early in the spring the amount of soluble material in this section of the soils was very limited. Later, during the summer months, the concentration of the soil solution increased in most of the soils, but decreased again in the late summer or fall. The variations in concentration were not so regular in the case of the virgin soils as they were for the field soils. The data as a whole, however, are in accord with those previously reported with the exception that in 1918 the maximum concentration was reached in June or July, while in 1919 this did not occur until somewhat later.

The data for the 6 to 12-inch sections are shown in table 2.

The concentration of the soil solution in the 6 to 12-inch stratum or so-called subsoil showed slight variations from month to month but no tendency to attain a maximum. These data are also in accord with the observations of 1918.

The data for the $\frac{1}{4}$-inch section show much more variation and offer an opportunity for interesting study. The results are included in table 3.

The data for the $\frac{1}{4}$-inch sections are very interesting inasmuch as they show a great variation in concentration from month to month. As noted in 1918 there is a strong tendency for an accumulation of soluble material to occur in this layer especially during periods of light or no rainfall. This material may be drawn from the lower sections by water movements. Rainfall undoubtedly affects these accumulations at the surface, light showers followed by high temperatures possibly permit further movements to the surface at the expense of the layer of soil immediately beneath, while heavy rains may result in a carrying of the soluble material to a considerable depth. Some data on this point have been presented (earlier publications) by McCool and Millar (1) and by Bouyoucos and McCool (2). This phase of the study will receive

TABLE 1

Soluble material in the ½ to 6-inch section of soils free of vegetation, expressed in terms of freezing point depression

SOIL TYPE	MARCH 24	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24
Virgin soil								
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Coloma loamy sand	0.008	0 010	0.007	0.003	0.007	0.003	0.001	0.001
Miami sandy loam	0.004	0.008	0.007	0.007	0.004	0.022	0.007	0.009
Clyde sandy loam	0.014	0.010	0.009	0.010	0.009	0.009	0.008	0.011
Miami sandy loam (light phase)		0.006	0.004	0.003	0.016	0.002		
Miami very fine sandy loam		0.001	0.002	0.005	0.008	0.008	0.008	0.008
Miami silt loam	0.010	0.008	0.009	0.008	0.021	0.017	0.005	0.012
Miami silt loam, no. 2	0.004	0.012	0.005	0.004	0.002	0.004	0.005	0.002
Field soils								
Coloma loamy sand	0.005	0.003	0.007	0.006		0.002	0.002	0.002
Miami sandy loam	0.007	0.012	0.002	0.007	0.018	0.011	0.011	0.003
Clyde sandy loam	0.005	0 005	0.006	0.006	0.006	0.032	0.028	0.003
Miami sandy loam (light phase)		0 008	0.007	0.002	0.009	0.008	0.000	0.006
Miami very fine sandy loam	0.009	0.008	0.006	0.006	0.011	0.020	0.020	0.010
Miami silt loam	0.009	0.005	0.004	0.009	0.016	0.008	0.008	0.001
Miami silt loam no. 2	0.008	0.007	0.003	0.006	0.017	0.002	0.007	0.012

TABLE 2

Soluble material in the 6 to 12-inch section of soils free of vegetation, expressed in terms of freezing point depression

SOIL TYPE	MARCH 24	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24
Virgin soil								
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Coloma loamy sand	0.008	0.009	0.000	0.003	0.003	0.001	0.001	0.010
Miami sandy loam	0.007	0.000	0.004	0.010	0.002	0.002	0.008	0.005
Clyde sandy loam	0.011	0.006	0.001	0.010	0.005	0.002	0.008	0.002
Miami sandy loam (light phase)		0.007	0.001	0.002	0.003	0.002		
Miami very fine sandy loam	0.010	0.001	0.002		0.005	0.001	0.001	0.002
Miami silt loam	0.011	0.002	0.004	0.005		0.010	0.008	0.005
Miami silt loam, no. 2	0.002	0.004	0.001	0.002	0.010	0.001	0.002	0.003
Field soil								
Coloma loamy sand	0.006	0.002	0.003	0.003	0.009	0.001	0.001	0.001
Miami sandy loam	0.009	0.001	0.004	0.008	0.003	0.009	0.006	0.001
Clyde sandy loam	0.009	0.005	0.000	0.002	0.003	0.006	0.004	0.003
Miami sandy loam (light phase)		0.002	0.001	0.002	0.003	0.002	0.000	0.002
Miami very fine sandy loam	0.010	0.006	0.000	0.003	0.006	0.002	0.008	
Miami silt loam	0.012	0.000	0.004	0.002	0.003		0.002	0.001
Miami silt loam, no. 2	0.002	0.006	0.004	0.003	0.002	0.002	0.007	0.004

further consideration later in this paper. For reference, the daily precipitation for the period of sampling is given in table 4.

The influence of vegetation of various kinds on the accumulation of soluble material in various sections of the soil and the subsequent movements of these soluble substances was also studied. The data in table 5 from some of the soils studied are representative.

Vegetation exerts a marked effect upon the accumulation and movement of salts in the soil. A study of the data for 1919 presented in table 4 brings out the following points. When grass or any of the common crops are present the

TABLE 3

Soluble material in the ¼-inch section of soils free of vegetation, expressed in terms of freezing point depressions

SOIL TYPE	MARCH 21	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24
Virgin soil								
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Coloma loamy sand	0.006	0.016	0.020	0.032		0.010	0.018	0.009
Miami sandy loam	0.003	0.018	0.032	0.040	0.012	0.066	0.030	0.030
Clyde sandy loam	0.008	0.020	0.032	0.029	0.008	0.018	0.028	0.011
Miami sandy loam (light phase)		0.010	0.013	0.008	0.011	0.006		
Miami very fine sandy loam	0.006	0.004	0.012	0.053	0.039	0.093	0.123	0.075
Miami silt loam	0.010	0.024	0.055	0.037	0.061	0.145	0.101	0.192
Miami silt loam, no. 2	0.010	0.010	0.014	0.006	0.008	0.003	0.009	0.011
Field soil								
Coloma loamy sand	0.004	0.005	0.015	0.014	0.026	0.002	0.015	0.010
Miami sandy loam	0.004	0.020	0.040	0.057	0.069	0.049	0.056	
Clyde sandy loam	0.004	0.023	0.055	0.058	0.068	0.060	0.101	0.071
Miami sandy loam (light phase)	0.009	0.006	0.008	0.009	0.012	0.003	0.015	
Miami very fine sandy loam	0.010	0.029	0.020		0.033	0.215	0.088	0.185
Miami silt loam	0.013	0.013	0.017	0.018	0.022	0.041	0.030	0.021
Miami silt loam, no. 2	0.008	0.006	0.017	0.018	0.011	0.010	0.024	0.056

accumulation of salts at the surface is largely prevented. Also such vegetable growth influences the concentration of the soil solution in the ¼ to 6-inch section and to some extent in the 6 to 12-inch stratum. These results are in accord with the findings for the previous year.

It will be noted that in both 1918 and 1919 the samples from the ¼ to 6-inch section of the field soils free of vegetation tended to show a somewhat greater accumulation of salts than the corresponding samples from the fence rows. This seemed rather unusual, inasmuch as the latter soils contained more organic matter; a possible explanation being the more thorough mixing of the organic matter in the field soils. To throw some light on this question plots along the

fences were scraped free of grass and then thoroughly hoed to a depth of 6 inches in order to thoroughly incorporate the organic matter in the surface soil. The data are presented in table 6.

A consideration of the data shows a great variation in concentration of the soil solution from time to time, especially in the case of the ½-inch section.

TABLE 4

Daily precipitation, 1919

DATE	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER
	inches	*inches*	*inches*	*inches*	*inches*	*inches*	*inches*	*inches*
1	T*		0.85					0 01
2								
3		0.16	1.46			T		
4	0.40		0.95			2.19	0.01	0.01
5	0.03	T		T	0.04	0 35		0.15
6	T	0.09		0.06				
7		0.70	T	0.27				
8	0.30	0.03	0.15					
9	1.11	0.26			0 05		T	0.07
10	0.01	0.28	T				0.21	0.45
11		T	T	0.21			0.01	
12		0.01		0.01	0.51			
13	T					T		
14		0.02	0 09		0.13	T	0.01	T
15	0.56	1.17	0.33	T		T		0.01
16	0.23	0.77	0.09	0.22		0.66		0.06
17	0.39	0.04	T			0 01		
18						0.07	0.01	
19			T	0 81			0.39	
20		0.04	0.12	0.05	0 06	0.02	0.43	0.03
21			0.01		0.06	0.08	0.54	0.01
22			0.19					0.01
23		0.34	0.05		T			
24		T		1.04				
25		T		0.46				0.13
26	0.08			0.05	0.30	0.04		0.15
27		0.11		T	0.20			0.23
28		0.11			0.11		0.02	0.02
29	0.19					0.58	0.69	0.13
30	0.18	T			0.17		0.29	0.72
31					0.06	0.03		0.81

*T = trace.

It is interesting to note, however, that there is no constant difference in favor of the soil maintained under any one of the conditions represented. This is true for every section of the soils studied and emphasizes the fact that there are many factors influencing the production and movement of soluble material in field soils.

TABLE 5

Effect of plant growth on the amount of soluble material in various soils during the season of 1919, expressed in terms of freezing point depressions

SOILS	MARCH 24	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24
Coloma loamy sand	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Virgin soil free of vegetation								
¼ inch section	0.006	0.016	0.020	0.032		0.010	0.018	0.009
¼–6 inch section	0.008	0.010	0.007	0.003	0.007	0.003	0.001	0.001
6–12 inch section	0.008	0.009	0.001	0.003	0.003	0.001	0.001	0.010
Virgin soil under sod								
¼ inch section	0.012	0.011	0.006	0.003	0.010	0.009	0.002	0.051
¼–6 inch section	0.008	0.009	0.002	0.004	0.006	0.004	0.002	0.006
6–12 inch section	0.007	0.003	0.001	0.001	0.001	0.002	0.001	0.008
Field soil free of vegetation								
¼ inch section	0.004	0.005	0.015	0.014	0.026	0.002	0.015	0.010
¼–6 inch section	0.005	0.003	0.007	0.006		0.002	0.002	0.002
6–12 inch section	0.006	0.002	0.003	0.003	0.009	0.001	0.001	0.001
Field soil growing wheat								
¼ inch section	0.005	0.008	0.005	0.002	0.008	0.003	0.008	0.009
¼–6 inch section	0.011	0.003	0.001	0.006	0.004	0.001	0.003	0.001
6–12 inch section	0.009	0.007	0.004	0.002	0.009	0.001	0.001	0.001
Timothy followed by corn								
¼ inch section			0.003	0.042		0.003	0.050	0.031
¼–6 inch section			0.003	0.005		0.003	0.003	0.001
6–12 inch section			0.001	0.007		0.001	0.001	0.008
Miami sandy loam								
Virgin soil free of vegetation								
¼ inch section	0.003	0.018	0.032	0.040	0.012	0.066	0.030	0.030
¼–6 inch section	0.004	0.008	0.007	0.007	0.004	0.022	0.007	0.009
6–12 inch section	0.007	0.001	0.004	0.010	0.002	0.002	0.008	0.005
Virgin soil under sod								
¼ inch section	0.012	0.006	0.005	0.022	0.013	0.011	0.009	0.013
¼–6 inch section	0.006	0.007	0.003	0.002	0.005	0.004	0.003	0.005
6–12 inch section	0.003	0.003	0.004	0.003	0.003	0.001	0.003	0.001
Field soil free of vegetation								
¼ inch section	0.004	0.020	0.040	0.057	0.069	0.049	0.056	
¼–6 inch section	0.007	0.012	0.002	0.007	0.018	0.011	0.011	0.003
6–12 inch section	0.009	0.001	0 004	0.008	0.003	0.009	0.006	0.001
Field soil growing timothy followed by corn								
¼ inch section	0.005	0.002	0.009	0.002	0.011	0.009	0.005	0.003
¼–6 inch section	0.008	0.007	0.003	0.004	0.009	0.006	0.003	0.001
6–12 inch section	0.008	0.002	0.001	0.001	0.009	0.005	0.001	0.001
Field soil growing clover								
¼ inch section		0.010	0.010	0.001	0.009		0.002	0.009
¼–6 inch section		0.008	0.001	0.002	0.006		0.003	0.003
6–12 inch section		0.006	0.008	0.003	0.002		0.004	0.003

TABLE 5—*Continued*

SOILS	MARCH 24	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Field soil growing oats								
¼ inch section			0.050	0.004	0.012	0.006	0.014	0.022
¼–6 inch section			0.004	0.003	0.011	0.004	0.010	0.001
6–12 inch section			0.008	0.002	0.005	0.007	0.003	0.005
Clyde sandy loam								
Virgin soil free of vegetation								
¼ inch section	0.008	0.020	0.032	0.029	0.008	0.018	0.028	0.011
¼–6 inch section	0.014	0.010	0.009	0.010	0 009	0.009	0.008	0.011
6–12 inch section	0.011	0.006	0.001	0.010	0.005	0.002	0.008	0.002
Virgin soil under sod								
¼ inch section	0.020	0.007	0.011	0.007	0.008	0.011	0.008	0.012
¼–6 inch section	0.010	0.010	0.005	0.008	0.006	0.006	0.009	0.003
6–12 inch section	0.013	0.005	0.008	0.008	0.003	0.002	0.003	0.002
Field soil free of vegetation								
¼ inch section	0.004	0.023	0.055	0.058	0.068	0.060	0.101	0.044
¼–6 inch section	0.005	0.005	0.006	0.006	0.006	0.032	0.028	0.003
6–12 inch section	0.009	0.005	0.001	0.002	0.003	0.006	0.004	0.003
Field soil growing wheat								
¼ inch section	0.004	0.005	0.009	0.009	0.013	0.018		0.020
¼–6 inch section	0.005	0.006	0.001	0.011	0.013	0.010		0.003
6–12 inch section	0.008	0.008	0.001	0.003	0.011	0.011		0.001
Miami very fine sandy loam								
Virgin soil free of vegetation								
¼ inch section	0.006	0.004	0.012	0.053	0.039	0.093	0.123	0.075
¼–6 inch section		0.001	0.002	0.005	0.008	0.008	0.008	0.008
6–12 inch section	0.010	0.001	0.001		0.005	0.001	0.001	0.001
Virgin soil under grass								
¼ inch section	0.018	0.006	0.009	0.004	0.020	0.008	0.012	0.033
¼–6 inch section	0.012	0.010	0.001	0.005	0.008	0.009	0.004	0.002
6–12 inch section	0.007	0.001	0.001	0.004	0.002	0.002	0.004	0.001
Field soil free of vegetation								
¼ inch section	0.010	0.029	0.020	0.186	0.033	0.215	0.088	0.185
¼–6 inch section	0.009	0.008	0.006	0.006	0.011	0.020	0.020	0.010
6–12 inch section	0.010	0.006	0.001	0.003	0.006	0.002	0.008	
Timothy and clover sod								
¼ inch section	0.010	0.007	0.009	0.004	0.018	0.023	0.020	0.012
¼–6 inch section	0.010	0.002	0.004	0.003	0.006	0.003	0.006	0.004
6–12 inch section	0.006	0.002	0.002	0.001	0.010	0.001	0.008	0.001
Miami silt loam								
Virgin soil free of vegetation								
¼ inch section	0.010	0.024	0.055	0.037	0.061	0.145	0.101	0.192
¼–6 inch section	0.010	0.008	0.009	0.008	0.021	0.017	0.005	0.012
6–12 inch section	0.011	0.002	0.004	0.005	0.028	0.010	0.008	0.005

TABLE 5—*Concluded*

SOILS	MARCH 24	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Virgin soil under grass								
¼ inch section	0.018	0.008	0.009	0.004	0.010	0.008	0.009	0.010
¼–6 inch section	0.007	0.010	0.002	0.001	0.011	0.004	0.002	0.001
6–12 inch section	0.011	0.002	0.002	0.001	0.004	0.003	0.001	0.007
Field soil free of vegetation								
¼ inch section	0.013	0.013	0.017	0.018	0.022	0.041	0.030	0.021
¼–6 inch section	0.009	0.005	0.004	0.009	0.016	0.008	0.008	0.001
6–12 inch section	0.012	0.001	0.004	0.002	0.003		0.002	0.001
Field soil under alsike sod								
¼ inch section	0.015	0.010	0.030	0.001	0.014	0.010	0.020	0.007
¼–6 inch section	0.007	0.002	0.008	0.005	0.007	0.008	0.008	0.001
6–12 inch section	0.008	0.002	0.002	0.001	0.002	0.005	0.001	0.002
Field soil under corn								
¼ inch section			0.026	0.049	0.098	0.010	0.018	0.018
¼–6 inch section			0.007	0.008	0.028	0.007	0.019	0.011
6–12 inch section			0.010	0.006	0.002	0.003	0.002	0.002

TABLE 6

Comparison of amounts of soluble material in areas of virgin, virgin cultivated, and field soils free of vegetation, expressed in terms of freezing point depressions

SOIL AND DEPTH OF SAMPLE	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24	AVERAGE
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Coloma loamy sand								
Virgin soil								
¼ inch section	0.016	0.020	0.032		0.010	0.018	0.009	0.0174
¼–6 inch section	0.010	0.007	0.003	0.007	0.003	0.001	0.004	0.0050
6–12 inch section	0.009	0 000	0.003	0.003	0.001	0.001	0.010	0.0038
Virgin soil cultivated								
¼ inch section	0.012	0.035	0.016	0.017	0.002	0.010	0.010	0.0145
¼–6 inch section	0.011	0.004	0.006	0.003	0.002	0.002	0.001	0.0041
6–12 inch section	0.009	0.000	0.005	0.001	0.002	0.001	0.000	0.0025
Field soil								
¼ inch section	0.005	0.015	0.014	0.026	0.002	0.015	0.010	0.0124
¼–6 inch section	0.003	0.007	0.006	0.010	0.002	0.002	0.002	0.0044
6–12 inch section	0.002	0.003	0.003	0.009	0.001	0.001	0.000	0.0027
Miami sandy loam								
Virgin soil								
¼ inch section	0.018	0.032	0.040	0.012	0.066	0.030	0.030	0.0289
¼–6 inch section	0.008	0.007	0.007	0.004	0.022	0.007	0.009	0.0086
6–12 inch section	0.000	0.004	0.010	0.002	0.002	0.008	0.005	0.0047

TABLE 6—*Concluded*

SOIL AND DEPTH OF SAMPLE	APRIL 26	MAY 28	JUNE 30	JULY 26	AUGUST 23	SEPTEMBER 26	OCTOBER 24	AVERAGE
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Virgin soil cultivated								
¼ inch section	0.010	0.030	0.051	0.035	0.040	0.032	0.022	0.0314
¼–6 inch section	0.009	0.004	0.014	0.015	0.016	0.021	0.013	0.0131
6–12 inch section	0.004	0.005	0.004	0.003	0.012	0.019	0.006	0.0076
Field soil								
¼ inch section	0.020	0.040	0.057	0.069	0.049	0.056		0.0485
¼–6 inch section	0.012	0.002	0.007	0.018	0.011	0.011	0.003	0.0091
6–12 inch section	0.001	0.004	0.008	0.003	0.009	0.006	0.001	0.0046
Clyde sandy loam								
Virgin soil								
¼ inch section	0.020	0.032	0.029	0.008	0.018	0.028	0.011	0.0209
¼–6 inch section	0.010	0.009	0.010	0.009	0.009	0.008	0.011	0.0094
6–12 inch section	0.006	0.001	0.010	0.005	0.002	0.008	0.002	0.0049
Virgin soil cultivated								
¼ inch section	0.020	0.024	0.014	0.013	0.021	0.021	0.021	0.0191
¼–6 inch section	0.012	0.011	0.012	0.016	0.013	0.012	0.002	0.0111
6–12 inch section	0.004	0.008	0.005	0.002	0.008	0.002	0.000	0.0041
Field soil								
¼ inch section	0.023	0.055	0.058	0.068	0.060	0.101	0.044	0.0584
¼–6 inch section	0.005	0.006	0.006	0.006	0.032	0.028	0.003	0.0123
6–12 inch section	0.005	0.000	0.002	0.003	0.006	0.004	0.003	0.0033
Miami silt loam								
Virgin soil								
¼ inch section	0.024	0.055	0.037	0.061	0.145	0.101	0.192	0.0878
¼–6 inch section	0.008	0.009	0.008	0.021	0.017	0.005	0.012	0.0114
6–12 inch section	0.002	0.004	0.005	0.028	0.010	0.008	0.005	0.0088
Virgin soil cultivated								
¼ inch section	0.004	0.066	0.053	0.038	0.072	0.024	0.071	0.0468
¼–6 inch section	0.005	0.012	0.016	0.024	0.020	0.019	0.011	0.0153
6–12 inch section	0.005	0.007	0.010	0.007	0.003	0.007	0.008	0.0067
Field soil								
¼ inch section	0.013	0.017	0.018	0.022	0.041	0.030	0.021	0.0231
¼–6 inch section	0.005	0.004	0.009	0.016	0.008	0.008	0.001	0.0073
6–12 inch section	0.000	0.004	0.002	0.003		0.002	0.001	0.0020
Miami very fine sandy loam								
Virgin soil								
¼ inch section	0.004	0.012	0.053	0.039	0.093	0.123	0.075	0.0570
¼–6 inch section	0.001	0.002	0.005	0.008	0.008	0.008	0.008	0.0057
6–12 inch section	0.000	0.000		0.005	0.001	0.000	0.000	0.0010
Virgin soil cultivated								
¼ inch section	0.007	0.012	0.035	0.016	0.032	0.019	0.040	0.0230
¼–6 inch section	0.010	0.008	0.008	0.004	0.003	0.007	0.005	0.0064
6–12 inch section	0.002	0.003	0.001	0.007	0.002	0.006	0.001	0.0031
Field soil								
¼ inch section	0.029	0.020	0.186	0.033	0.215	0.088	0.185	0.1080
¼–6 inch section	0.008	0.006	0.006	0.011	0.020	0.020	0.010	0.0116
6–12 inch section	0.006	0.000	0.003	0.006	0.002	0.008		0.0040

RESULTS FOR 1920

For the 1920 studies it was deemed advisable to change the depths of sampling somewhat in order to observe more closely the effects of rainfall on the salt content of the soil to approximately the depth of plowing. Accordingly the following soil strata were sampled 0 to ¼-inch; ¼ to 3-inch; 3 to 9-inch. The dates of sampling were also chosen with reference to climatic conditions instead of sampling monthly as was done previously. It was further found desirable to omit two of the soils previously included in these studies.

In studying the effect of rainfall on the accumulation of salts in the various soil strata and their movement from zone to zone it is only possible to consider the plots on the virgin soil maintained free of vegetation since those in the field were subject to various tillage operations. The data for these plots are presented in table 7 and the precipitation record covering the period of sampling is found in table 8.

A consideration of the data from the uncultivated plots shows that the moist weather preceding July 30 resulted in a decrease of the salt content of the ¼-inch stratum of three of the soils, the variation in the other being negligible. The results from the hoed plots are of no value for this date since these plots were given a thorough hoeing a few days before sampling and sufficient time had not elapsed for the distribution of salts to become adjusted.

The heavy precipitation preceding August 18 caused a further decrease in the accumulation of salts in the ¼-inch section of the soils, the Miami sandy loam varying somewhat from the other samples in this case. An increased movement of salts to the surface resulted from the dry period preceding October 5, with one exception, the hoed plot of Coloma loamy sand showing a decrease. This increase was in turn followed by a decrease in concentration of soluble material as a result of the rains shortly before December 3, the Miami silt loam being an exception.

The data for the ¼ to 3-inch sections show a considerable variation but a general tendency toward an increase of solubles for the October sampling. This would indicate a tendency for salts to move into this zone as a result of the dry weather preceding this date. For the 3 to 9-inch stratum an average of results shows an increase in freezing point depression on July 30 and October 5 with a decrease for August 18. It would appear, therefore, that the lighter rains preceding the July sampling had caused an increased production or movement of salts into this zone as had also the dry period preceding October 5; while the heavier rains during August had resulted in the washing of salts below this depth.

In considering these data it should be borne in mind that these plots are somewhat widely separated and that none of them lie within a mile of the rain gauge. In consequence there is opportunity for somewhat wide variations in the amount of precipitation received.

TABLE 7

Influence of rainfall on the distribution of soluble material in field soils, expressed in freezing point depressions

SOIL AND DEPTH OF SAMPLE	JULY 20	JULY 30	AUGUST 18	OCTOBER 5	DECEMBER 3
Coloma loamy sand	°C.	°C.	°C.	°C.	°C.
Uncultivated					
¼ inch section	0.012	0.013	0.006	0.015	0.010
¼–3 inch section	0.010	0.009	0.004	0.007	0.010
3–9 inch section	0.001	0.008	0.004	0.002	0.009
Previously hoed					
¼ inch section	0.006	0.060	0.034	0.016	0.010
¼–3 inch section	0.004	0.010	0.007	0.007	0.011
3–9 inch section	0.003	0.004	0.001	0.006	0.009
Miami sandy loam					
Uncultivated					
¼ inch section	0.040	0.020	0.030	0.081	
¼–3 inch section	0.006	0.011	0.012	0.030	
3–9 inch section	0.002	0.009	0.008	0.016	
Previously hoed					
¼ inch section	0.012	0.062	0.018	0.026	
¼–3 inch section	0.008	0.017	0.010	0.019	
3–9 inch section	0.001	0.008	0.011	0.016	
Clyde sandy loam					
Uncultivated					
¼ inch section	0.020	0.008	0.007	0.014	0.008
¼–3 inch section	0.009	0.004	0.004	0.008	0.006
3–9 inch section	0.004	0.002	0.002	0.004	0.008
Previously hoed					
¼ inch section	0.021	0.026	0.020	0.058	0.008
¼–3 inch section	0.009	0.002	0.010	0.021	0.008
3–9 inch section	0.004	0.010	0.006	0.011	0.008
Miami very fine sandy loam					
Uncultivated					
¼ inch section	0.024	0.018	0.014	0.020	0.010
¼–3 inch section	0.002	0.004	0.007	0.008	0.004
3–9 inch section	0.003	0.009	0.002	0.006	0.007
Previously hoed					
¼ inch section	0.030	0.018	0.013	0.015	0.008
¼–3 inch section	0.002	0.004	0.007	0.008	0.004
3–9 inch section	0.003	0.009	0.002	0.006	0.007
Miami silt loam					
*Uncultivated					
Previously hoed					
¼ inch section	0.027	0.024	0.004	0.018	0.018
¼–3 inch section	0.007	0.013	0.015	0.017	0.011
3–9 inch section	0.008	0.014	0.006	0.013	0.012

* This plot was accidentally destroyed.

The variation in the data also indicate that factors other than rainfall materially influence the distribution of the salts in field soils. It seems that texture, compaction and biological activities may also be important. A future paper will deal more in detail with this phase of the salt content of field soils.

TABLE 8

Daily precipitation, 1920

DATE	JULY	AUGUST	SEPTEMBER	OCTOBER	NOVEMBER	DECEMBER
	in.	*in.*	*in.*	*in.*	*in.*	*in.*
1	T*				0.35	0.70
2	0.05				0.21	T
3				0.02	0.01	
4						0.81
5	T	T	0.02			0.03
6	0.24	0.62			T	
7	T				0.02	
8	0.60				0.10	
9	0.03	0.24	0.05		0.09	0.06
10		T		0.01	T	0.16
11			T		T	0.01
12					T	
13	0.23	0.48			T	0.27
14	0.16				0.01	0.34
15			0.58	0.01	0.01	0.08
16		0.15		0.01	0.14	T
17						0.02
18	1.40				T	0.02
19						0.03
20			0.07	0.01		T
21	T	0.33			0.19	0.18
22					0.79	0.80
23	T				0.03	0.06
24	T		0.02	0.08	0.14	0.02
25				0.11	0.02	T
26		T	0.13	0.59	0 06	0.29
27		T	0.39	0.47	T	0.03
28	0.01					0.01
29	0.07	0.18	T	T	T	
30	0.14		T		0.07	0.01
31	0.08			0.06		0.01

* T = trace.

During the season of 1920 samples were not collected under as great a variety of crops as in previous years. The results of the freezing point determinations on the samples collected are given in table 9.

The tendency for vegetation to prevent the large accumulation of salts at the surface is again noticed in the data above. This substantiates the observations of the two previous years. It will be observed in some cases, however,

TABLE 9

Influence of vegetation on the accumulation and movement of salts in field soils, expressed in terms of freezing point depressions

TYPE AND CONDITION OF SOIL	JULY 30			AUGUST 18			OCTOBER 5			DECEMBER 3		
	¼"	¼-3"	3-9"	¼"	¼-3"	3-9"	¼"	¼-3"	3-9"	¼"	¼-3"	3-9"
	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Coloma loamy sand												
Virgin soil free of vegetation	0.013	0.009	0.008	0.006	0.004	0.004	0.015	0.007	0.002	0.010	0.010	0.009
Virgin sod	0.016	0.011	0.002	0.007	0.012	0.001	0.016	0.012	0.008	0.012	0.011	0.012
Field soil free of vegetation	0.011	0.005	0.005				0.005	0.004	0.001	0.010	0.008	0.010
Clover field	0.011	0.011	0.009	0.008	0.004	0.004	0.012	0.003	0.005	0.010	0.008	0.011
Miami sandy loam												
Virgin soil free of vegetation	0.020	0.011	0.009	0.030	0.012	0.008	0.081	0.030	0.016			
Virgin sod	0.010	0.005	0.001	0.010	0.005	0.002	0.018	0.010	0.007			
Field soil free of vegetation	0.170	0.019	0.011	0.008	0.002	0.015	0.037	0.018	0.018			
Timothy sod	0.008	0.005	0.005	0.003	0.003	0.001	0.019	0.016	0.014			
Corn following clover	0.070	0.005	0.012	0.007	0.003	0.012	0.018	0.008	0.017			
Oats	0.012	0.006	0.006	0.006	0.003	0.012	0.018	0.018	0.016			
Clyde sandy loam												
Virgin soil free of vegetation	0.008	0.004	0.002	0.007	0.004	0.002	0.014	0.008	0.004	0.008	0.006	0.008
Virgin sod	0.016	0.008	0.005	0.018	0.002	0.002	0.008	0.005	0.007	0.013	0.009	0.011
Field soil free of vegetation	0.018		0.007	0.014	0.005	0.002	0.025	0.008	0.004			
Clover	0.020	0.009	0.006	0.010	0.004	0.003	0.018	0.012	0.003			
Miami very fine sandy loam												
Virgin soil free of vegetation	0.018	0.004	0.009	0.014	0.007	0.002	0.020	0.008	0.006	0.010	0.004	0.007
Virgin sod	0.013	0.008	0.005	0.018	0.007	0.006	0.011	0.005	0.002	0.008	0.007	0.002
Field soil free of vegetation	0.007	0.005	0.010	0.017	0.008	0.007	0.006	0.003	0.005	0.008	0.008	0.008
Timothy sod	0.012	0.008	0.004	0.004	0.002	0.002	0.009	0.008	0.004	0.006	0.003	0.009
Miami silt loam												
*Virgin soil free of vegetation												
Virgin sod	0.018	0.008	0.006	0.019	0.005	0.004	0.016	0.008	0.009	0.017	0.012	0.007
Field soil free of vegetation	0.136	0.008	0.009	0.087	0.013	0.008	0.105	0.044	0.018			
Corn after alsike sod	0.114	0.016	0.013	0.006	0.005		0.027	0.014	0.010	0.012	0.008	0.006
Oats—stubble	0.007	0.002	0.005	0.012	0.008	0.002	0.014	0.011	0.010			

* This plot was accidentally destroyed.

TABLE 10

Comparative rate of formation of salts in cultivated and uncultivated soils free of vegetation, expressed in terms of freezing point depression

SOIL	JULY 20			JULY 30			AUGUST 18			OCTOBER 5			DECEMBER 3		
	¼"	¼ 3"	3 9"	¼"	¼-3"	3-9"	¼"	¼-3"	3-9"	¼"	¼-3"	3-9"	¼"	¼-3"	3-9"
	°C.	°C,	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Coloma loamy sand															
Virgin scraped	0.012	0.010	0.001	0 013	0.009	0.008	0.006	0.004	0.004	0.015	0.007	0.002	0.010	0.010	0.009
Virgin hoed	0.006	0.004	0 003	0.060	0.010	0.004	0.034	0.007	0.001	0.016	0.007	0.006	0.010	0.011	0.009
Miami sandy loam															
Virgin scraped	0.040	0.006	0.002	0.020	0.011	0 009	0.030	0.012	0.008	0.081	0.030	0.016			
Virgin hoed	0.012	0.008	0.001	0.062	0.017	0.008	0.018	0.010	0.011	0.026	0.019	0.016			
Clyde sandy loam															
Virgin scraped	0.020	0.009	0.004	0.008	0.004	0.002	0.007	0.004	0.002	0.014	0.008	0.004	0.008	0.006	0.008
Virgin hoed	0.021	0.009	0.004	0.026	0.002	0.010	0.020	0.010	0.006	0.058	0.021	0.011	0.008	0.008	0.008
Miami very fine sandy loam															
Virgin scraped	0.024	0.002	0.003	0.018	0.004	0.009	0.014	0.007	0.002	0 020	0.008	0.006	0.010	0.004	0.007
Virgin hoed	0.030	0.013	0.004	0 018	0.005	0.006	0.013	0.006	0.002	0.015	0.011	0.007	0.008	0.008	0.004
Miami silt loam															
Virgin scraped	0.020	0.010	0.004	0.110	0.040	0.005	0.048	0.032	0.009	0.028	0.023	0.006	0.012	0.009	0.010
Virgin hoed	0.027	0.007	0.008	0.024	0.013	0.014	0.004	0.015	0.006	0.018	0.017	0.013	0.018	0.011	0.012

that considerable soluble material was found at the surface of soil bearing certain crops which when carried below by rains would result in a stimulation of growth. This point has been referred to previously.

The data for the ¼ to 3-inch section show no consistent differences in the accumulation of soluble material as the result of plant growth. On October 5, however, the majority of the samples show more soluble salt in the uncropped soils. Since the first two samplings were made after periods of appreciable rainfall and the latter one October 5 after several days of practically no precipitation it seems that climatic conditions may be a factor. In the 3 to 9-inch sections the average of the results indicate a greater amount of soluble material in the plots devoid of vegetation. These results are substantially in accord with those for 1918 and 1919.

The influence of distributing the organic matter of several virgin soils through a somewhat thicker stratum by means of hoeing on the formation of soluble substances is shown in table 10.

The results are somewhat surprising in that they show no acceleration of the formation of solubles as a result of cultivation. These observations are in accord with those of last year but are interesting in that it seemed probable during the second year when more time had elapsed for decay to reach a more advanced stage that the production of soluble salts would be materially increased. It seems, therefore, that the tendency previously noted for more soluble material to accumulate in field soils free of vegetation than in the corresponding virgin soils, is not due to more thorough distribution of the organic matter or to increased aeration or distribution of organisms as a result of tillage.

SUMMARY

The data for 1919 afford additional evidence that the soluble salt content of the surface 6 inches of soils free of vegetation is quite low in the early spring and late fall but reaches a somewhat higher concentration sometime during the summer.

The salt content of the 6 to 12-inch section was usually quite low and showed no tendency to reach a maximum during summer.

Plant growth modified the amount of solubles in the ¼ to 6-inch section and tended to prevent the accumulation of soluble salts at the surface of the soil.

When no vegetation was present soluble substances tended to accumulate in the ¼-inch soil section, especially during dry periods.

The above observations offer further evidence in support of the conclusion previously published.

Rainfall was shown to be an important factor in the distribution of soluble materials in the soil strata. This problem is being investigated more in detail.

The data also indicate that factors other than rainfall materially influence the accumulation and distribution of salts in field soils.

The incorporation of the organic matter of several virgin soils throughout the surface 6-inch section by hoeing did not lead to a more rapid production of soluble material than was noted when these soils were maintained free of vegetation but not cultivated.

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ACID SOIL STUDIES: III. THE INFLUENCE OF CALCIUM CARBONATE, CALCIUM OXIDE, AND CALCIUM SULFATE ON THE SOLUBLE SOIL NUTRIENTS OF ACID SOILS

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This series of acid soil studies was undertaken to ascertain why some so-called "acid soils" of Oregon respond well to lime treatment while other acid soils do not show an increase in crop yields after the application of lime. Observations of both pot and field tests reveal the fact that even legumes, such as clover and field peas, do not show increased yields on certain limed acid soils referred to above. Various laboratory tests such as the determination of the acidity or lime requirement by several prevalent methods, chemical and physical analyses of the soils, and reactions with neutral salts do not disclose any particular abnormality in these soils. Consequently a more systematic study was undertaken to find some differential factor that would account for the unnatural action of those acid soils that do not respond to lime treatment.

In paper I (4) a study was made of the soil separates while in paper II (5) observations were made on the changes in calcium compounds added to the different types of acid soils, but no unusual results were obtained that would account for the anomalous behavior of some of them.

It is generally recognized that the application of lime to an acid soil improves its texture and creates a better medium for the optimum development of nitrifying and other beneficial organisms. Lime also supplies a necessary base and changes certain elements into a more available form. In promoting chemical and bacteriological functions it would necessarily change the composition of the soil solution. Since the applications of lime increased the crop yields on some of the soils under study while no effects were noted in others, it was thought that a study of the changes in the soluble soil nutrients of the several soils after treatment with lime might disclose information that would aid in solving the problem. Accordingly a study was made of the effects of calcium carbonate, calcium oxide, and calcium sulfate on the soluble nutrients of five different acid soils.

DESCRIPTION OF SOILS

The five so-called "acid soils" selected for study were representative of Willamette valley and coast lands of Oregon and varied greatly in their lime

requirement or acidity as indicated by the Veitch (8), Jones (3), and Hopkins (2) methods. To discriminate between the different soils they were given the laboratory numbers 11076, 11077, 11078, 11079 and 11080.

Soil 11076 is classified as a Willamette silt loam and shows a lime requirement of 3200 pounds of calcium carbonate per acre. This soil responds well to lime treatment and gave nearly 100 per cent increase in clover crop from the application of 1 ton of limestone per acre.

Soil 11077 is classified as a Salem gravelly loam and has a lime requirement of about 1 ton per acre. No increase in either clover, barley, or field peas was obtained by the application of lime to this soil.

Soil 11078 is also a Willamette silt loam and is almost identical with soil 11076 in texture and lime requirement. However, applications of lime did

TABLE 1

Physical analyses of soils

SOIL NUMBER	COARSE SAND	FINE SAND	SILT	CLAY
	per cent	*per cent*	*per cent*	*per cent*
11076	0.9	27.1	52.1	19.9
11077	25.6	42.0	22.5	9.9
11078	1.3	32.4	49.6	16.7
11079	28.5	26.5	29.2	15.8
11080	38.3	29.4	23.7	8.6

TABLE 2

The chemical analyses of soils

SOIL NUMBER	CaO	MgO	P_2O_5	K_2O	N	HUMUS
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
11076	0.69	0.11	0.35	2.50	0.213	2.35
11077	1.96	0.33	0.77	1.68	0.210	2.59
11078	0.53	0.24	0.22	3.03	0.216	2.35
11079	0.16	0.23	0.29	1.41	0.320	3.88
11080	0.34	0.41	0.07	0.79	0.364	4.60

not increase either clover or barley crops. This soil is located on the west border of the Willamette Valley on the Experiment Station farm while soil 11076 is 12 miles distant directly across the Willamette Valley and on its east border.

Soil 11079 is classified as a brown clay loam and has a lime requirement of 5 tons per acre. It responds well to lime treatment.

Soil 11080 is a medium sandy loam and is a representative type of a large area of coast lands. It has a very high lime requirement of over 10 tons to the acre. Applications of limestone at the low rate of 2 tons per acre gave more than 100 per cent increase in clover crop.

The following table shows the physical analyses of the different soils. The coarse and medium sand were combined and listed as coarse sand, while the fine sand and very fine sand were combined and listed as fine sand.

Chemical analyses reporting the percentage of essential plant food elements are given in table 2.

It is apparent from the above analyses that all of the soils under investigation are deficient in both calcium and magnesium with, perhaps, the exception of soil 11077. On account of the small amount of these elements present in the soil it would seem that all of them would respond to lime treatment. The other plant food elements are comparatively high and from their standpoint the soils may be judged fertile.

PROCEDURE

The five different acid soils described above were collected in the early spring when the nitrate content was low. After they had been air-dried, they were sifted through a 10-mesh sieve, which was accomplished by crushing the larger lumps with a rubber tipped pestle. Two-thousand-gram portions were then weighed out and sufficient calcium carbonate was thoroughly incorporated in each lot to satisfy the lime requirement as determined by the Veitch (8) method. Similar portions of each soil were also treated with calcium oxide and calcium sulfate in amounts equivalent to the calcium employed in the calcium carbonate-treated lot. Owing to the excessive amount necessary, soil 11080 received only one-half of the calcium sulfate equivalent to the amount of calcium carbonate used in that soil. Similar amounts of the different soils untreated were used as controls. The prepared soils were then transferred to large wide-mouthed jars and enough distilled water was added to bring each soil to its optimum moisture content. This percentage of moisture was maintained throughout the experiment. The jars were kept in a room the temperature of which varied between 15° and 20°C.

In order to observe the effects of the various treatments on the different soils, determinations were made periodically of the soluble soil nutrients. The first determinations of the soluble soil nutrients were made after the treated soils had stood 24 hours. For convenience this is designated series 1. Subsequent analyses were made after the treated soils had stood 3 months and 6 months and are referred to as series 2 and series 3, respectively. For the determination of the soluble soil nutrients a soil solution was prepared by shaking at intervals during 8 hours, 1 part of dry soil with 5 parts of distilled carbon-dioxide-free water. Immediately preceding the preparation of the soil solution, the moisture content of each soil was determined and allowance was made for the water present. The soil was then allowed to stand over night after which it was centrifuged at high speed to settle particles and finally passed through a Pasteur-Chamberland filter. Calcium, magnesium, potassium, phosphorus, sulfates, nitrates and total solids were then determined in the solutions thus obtained.

Calcium, phosphorus and potassium were determined by methods suggested by Stewart (6) slightly modified to suit the work at hand. It was found

advantageous to take larger portions of the soil solution than recommended by Stewart especially for phosphorus and magnesium. Sulfates were precipitated as barium sulfate in a 400 cc. aliquot of the soil solution slightly acidified with hydrochloric acid. Nitrates were determined colorimetrically by the phenol-di-sulfonic acid method. The hydrogen-ion concentration was measured by the gas-chain method but it was found that after the first series, constant readings could not be obtained on account of the high nitrate content which apparently was reduced by hydrogen forming ammonia.

TABLE 3

Series 1. Composition of the soil solutions 24 hours after treatment

SOIL NUMBER	TREATMENT		PARTS PER MILLION OF SOIL SOLUTION						
	Material	Quantity	Solids	CaO	MgO	K_2O	P_2O_5	SO_3	NO_3
		per cent							
11076	Control		142.0	21.1	7.78	7.74	1.70	3.1	57.2
11076	$CaCO_3$	0.32	196.0	46.3	11.76	3.20	1.85	3.1	57.2
11076	CaO	0.18	167.0	35.9	8.32	4.31	1.71	3.1	54.7
11076	$CaSO_4 \cdot 2H_2O$	0.55	879.0	249.0	42.71	9.88	0.47	420.0	54.7
11077	Control		58.5	10.2	4.16	4.55	1.68	2.6	3.2
11077	$CaCO_3$	0.18	93.5	25.4	6.70	5.91	1.70	2.6	3.2
11077	CaO	0.10	91.0	23.7	6.52	5.81	1.65	5.2	3.2
11077	$CaSO_4 \cdot 2H_2O$	0.30	573.5	153.8	19.72	13.15	1.16	257.3	1.6
11078	Control		87.0	13.4	4.79	3.68	0.48	1.7	31.2
11078	$CaCO_3$	0.32	137.0	36.6	7.69	3.58	0.62	1.9	28.0
11078	CaO	0.18	132.0	28.4	5.79	3.24	0.81	3.1	28.4
11078	$CaSO_4 \cdot 2H_2O$	0.55	905.0	278.5	38.56	5.47	0.54	461.7	26.4
11079	Control		33.0	5.68	2.54	3.00	0.34	Trace	7.6
11079	$CaCO_3$	0.62	151.0	56.4	4.34	3.20	0.58	6.8	7.6
11079	CaO	0.35	116.0	30.8	1.90	1.55	0.54	7.9	6.0
11079	$CaSO_4 \cdot 2H_2O$	1.14	1429.0	459.5	57.35	6.60	0.31	790.6	5.2
11080	Control		125.0	13.9	6.50	6.40	0.27	Trace	5.9
11080	$CaCO_3$	1.55	354.5	115.0	15.65	6.90	0.39	4.8	9.6
11080	CaO	0.87	243.5	48.3	6.35	4.85	0.76	5.0	5.9
11080	$CaSO_4 \cdot 2H_2O$	1.34	1527.8	451.0	63.00	18.60	0.39	800.0	3.7

The analyses of the soil solutions made after 24 hours, after 3 months and after 6 months are reported in tables 3, 4 and 5, respectively. Since utmost precautions were taken to prepare the soil solutions of all soils for the three different series in a similar manner as described above and since it is desirable to compare the concentration of the soluble soil nutrients in the soil solution, the results in the following tables and all subsequent tables are reported as parts per million of the soil solution.

DISCUSSION

The results obtained in the first series, as reported in table 3, where the soil solution was prepared 24 hours after treatment shows mainly the chemical action of the different treatments on the solubility of the soil nutrients since adequate time had not elapsed to permit any beneficial or toxic effects on the soil organisms. In general there were no significant chemical reactions that would indicate an abnormal condition in any of the soils. As would be expected, the amount of solids or total soluble salts was greater in the treated

TABLE 4

Series 2. Compostion of soil solutions 3 months after treatments

SOIL NUMBER	TREATMENT		PARTS PER MILLION OF SOIL SOLUTION						
	Material	Quantity	Solids	CaO	MgO	K_2O	P_2O_5	SO_3	NO_3
		per cent							
11076	Control		179.5	26.4	10.32	7.45	1.93	3.4	78.0
11076	$CaCO_3$	0.32	197.0	45.2	9.80	5.23	0.97	4.5	84.0
11076	CaO	0.18	193.5	42.8	11.05	5.42	0.70	4.6	90.8
11076	$CaSO_4 \cdot 2H_2O$	0.55	1005.5	285.5	50.50	11.34	0.48	455.0	90.4
11077	Control		83.0	14.4	4.98	6.30	1.97	3.4	30.8
11077	$CaCO_3$	0.18	98.0	20.7	4.61	4.94	1.06	3.4	30.8
11077	CaO	0.10	94.0	22.2	4.88	4.30	1.06	5.0	30.8
11077	$CaSO_4 \cdot 2H_2O$	0.30	452.5	68.6	17.24	8.52	0.46	212.0	22.8
11078	Control		111.5	20.7	7.78	3.78	1.01	10.3	26.4
11078	$CaCO_3$	0.32	132.0	26.2	7.06	2.18	0.81	3.3	40.0
11078	CaO	0.18	112.5	24.6	6.79	2.08	0.87	3.5	44.0
11078	$CaSO_4 \cdot 2H_2O$	0.55	909.0	283.6	42.55	4.60	0.57	450.0	33.2
11079	Control		55.5	7.7	3.71	4.65	0.41	Trace	17.2
11079	$CaCO_3$	0.62	138.5	37.5	1.99	2.52	0.43	7.4	43.6
11079	CaO	0.35	130.2	33.9	None	2.23	0.34	7.5	40.0
11079	$CaSO_4 \cdot 2H_2O$	1.14	1408.5	426.3	66.65	4.84	0.34	739.0	17.0
11080	Control		168.0	24.8	10.60	8.12	0.46	Trace	11.6
11080	$CaCO_3$	1.55	305.0	80.0	10.05	4.56	0.51	5.5	50.0
11080	CaO	0.87	326.0	82.0	9.90	5.04	0.64	5.7	43.6
11080	$CaSO_4 \cdot 2H_2O$	1.34	1638.0	471.5	66.50	15.85	0.33	816.5	0.9

soils than in the untreated controls. Any increase would represent the solubility of the substances used in the treatments and the solvent effects of the dissolved salts on the soil. Both calcium carbonate and calcium oxide treatments increased the soluble calcium in all soils, the former giving appreciably higher amounts, especially in soil 11080. The calcium carbonate treatment likewise increased the soluble magnesium in all soils while the calcium oxide treatment gave smaller increases in magnesium for soils 11076, 11077 and 11078 and slight decreases in soils 11079 and 11080. Even greater quantities

of magnesium were rendered soluble by the calcium sulfate treatment. The calcium sulfate treatments also increased the solubility of potassium in all soils which confirms similar results obtained by other workers. Attention is called to the abnormally low amounts of phosphates and sulfates which do not show differences worthy of note.

In the second series where the soil solution was prepared after chemical and biological activities had progressed 3 months more significant changes had occurred. The most important changes are seen in the effects of calcium

TABLE 5

Series 3. Composition of soil solutions 6 months after treatments

SOIL NUMBER	TREATMENT		PARTS PER MILLION OF SOIL SOLUTION						
	Material	Quantity	Solids	CaO	MgO	K_2O	P_2O_5	SO_3	NO_3
		per cent							
11076	Control		217.0	31.8	11.05	7.36	0.81	4.0	84.0
11076	$CaCO_3$	0.32	257.8	56.9	11.20	5.28	1.09	6.4	124.8
11076	CaO	0.18	237.8	50.0	12.45	6.01	1.19	5.7	116.0
11076	$CaSO_4 \cdot 2H_2O$	0.55	918.2	264.1	45.40	10.85	0.68	417.5	68.0
11077	Control		124.2	24.8	17.85	6.05	0.96	3.4	56.0
11077	$CaCO_3$	0.18	135.8	27.9	16.55	5.01	1.12	4.5	52.8
11077	CaO	0.10	140.0	29.3	17.75	5.76	0.96	6.0	55.2
11077	$CaSO_4 \cdot 2H_2O$	0.30	429.0	145.6	17.55	8.38	0.69	205.3	37.6
11078	Control		126.0	22.1	9.55	2.71	3.09	3.2	50.0
11078	$CaCO_3$	0.32	148.5	34.6	8.40	2.35	2.24	3.4	68.0
11078	CaO	0.18	162.0	31.8	6.15	1.79	2.32	4.6	67.2
11078	$CaSO_4 \cdot 2H_2O$	0.55	971.5	295.0	38.50	4.94	0.54	460.0	50.8
11079	Control		88.0	13.7	2.98	3.05	0.70	0.7	36.8
11079	$CaCO_3$	0.62	173.7	46.9	None	1.45	0.39	6.2	80.8
11079	CaO	0.35	174.2	46.9	None	1.21	0.12	6.0	80.0
11079	$CaSO_4 \cdot 2H_2O$	1.14	1560.2	441.0	66.40	5.85	None	755.0	36.0
11080	Control		309.5	39.9	17.30	8.18	0.15	Trace	58.0
11080	$CaCO_3$	1.55	444.8	105.5	13.70	5.33	0.37	7.7	171.2
11080	CaO	0.87	464.0	110.2	13.75	5.33	None	7.7	166.0
11080	$CaSO_4 \cdot 2H_2O$	1.34	1805.2	494.0	99.10	16.86	None	905.5	16.0

carbonate and calcium oxide on the production of nitrates in the different soils. In all five types the untreated controls showed an increase in nitrates which varied in amounts with the different soils. Nitrates developed in appreciable amounts in the controls of soils 11076 and 11077 but only to a very limited extent in soils 11078, 11079 and 11080. On the other hand the calcium carbonate and calcium oxide treatments of soils 11079 and 11080 increased the nitrates four-fold and seven-fold respectively, while soil 11077, which does not respond to lime applications, gave no increase in nitrates with similar

treatment. Soil 11078, which also does not respond to applications of lime. did not show a very great increase in the amount of nitrates formed in the calcium carbonate and calcium oxide treated pots. Again, soil 11076, which responds to applications of lime, showed a larger amount of nitrates in the calcium carbonate and calcium oxide treated pots than in the control. These results indicate that the nitrification processes are stimulated by calcium carbonate and calcium oxide in those acid soils that respond to lime treatment but the formation of nitrates is not so great in those soils that do not respond to lime treatment.

Further examination of table 4 shows that the calcium sulfate treatment increased the nitrates in soil 11076 but seemed to have a depressing effect on the nitrification processes in the others. No consistent changes are apparent in the other soluble soil nutrients that might indicate any differential characteristics.

Table 5 reports the amounts of soluble nutrients in the different soils 6 months after treatment. Again we note the favorable influence of calcium carbonate and calcium oxide on the development of nitrates in those soils that respond to lime treatment. As in series 2 the untreated controls of all soils showed an increase in nitrates. In soils 11076, 11079 and 11080, however, far greater amounts of nitrates were produced in the calcium carbonate and calcium oxide treated pots than in the controls. On the other hand, soil 11077 showed smaller amounts of nitrates in the calcium carbonate and calcium oxide treated pots than in the control and soil 11078 showed comparatively small increases in the treated pots. These results further substantiate those obtained in series 2, that the nitrification processes are greatly stimulated by calcium carbonate and calcium oxide in those soils that respond to lime treatment and to a less extent in those soils that do not respond to lime treatment.

As in the previous series no definite statements can be made regarding the effects of the different treatments on the other soluble soil nutrients. It will be observed that the total soluble salts increased over the amount found in series 2. With a few exceptions the soluble calcium and magnesium increased in both treated and untreated soils. Both phosphates and sulfates were low as in the first two series.

It is of interest to note that the effect of calcium sulfate treatment on the solubility of potassium was approximately constant throughout the three series. This indicates that the action of calcium sulfate on the solubility of potassium is a chemical reaction and is not influenced greatly by bacteriological changes.

Considering the results of the three series from the standpoint of a possible reason for two of the acid soils not responding to lime treatment in actual field tests, it is apparent that the nitrification processes and conditions that influence them are the most potent factors. The supply of an abundance of nitrates available at the right time would doubtlessly increase crop yields, while a deficiency would not permit optimum growth.

THE EFFECTS OF PHOSPHATES UPON NITRIFICATION

It is evident from the above results that the available phosphorus in all the soils is exceedingly low. Stoddart (7), and Conner (1) emphasized the need of acid soils in general for available phosphates. It is possible that the two acid soils under study which do not respond to lime treatment may contain excessive amounts of iron and aluminum salts and that the treatment with calcium carbonate or oxide does not destroy entirely their toxic properties sufficiently to permit favorable conditions for the optimum development of nitrifying organisms.

To learn whether the application of phosphates would overcome a possible toxicity and permit more rapid formation of nitrates, especially in soils 11077 and 11078, treatments of the different soils were made using mono-calcium phosphate, mono-calcium phosphate plus calcium carbonate, and tri-calcium phosphate. Convenient amounts of the soils were taken and the phosphates added at the rate of about 600 pounds per acre. A composite infusion prepared from the fresh soils was added to distilled water and was used to maintain the moisture content. The nitrates were determined in soils 11076, 11077, and 11078 after standing 6 weeks at 26° to 30°C. temperature while soils 11079 and 11080 stood 2 weeks. Table 6 records the treatment and amount of nitrates formed in parts per million of soil solution.

The results cited above present some interesting data. It will be observed that soil 11078, which does not respond to lime treatment, showed increased formation of nitrates when treated with mono-calcium phosphate and still greater amounts when treated with mono-calcium phosphate plus calcium carbonate. Calcium carbonate alone and the insoluble tri-calcium phosphate had no beneficial effects. On the other hand treatment of soils 11076, 11079 and 11080, with phosphates did not have a beneficial effect. In fact the mono-calcium phosphate had a depressing effect on the formation of nitrates. Substantiating previous results these soils showed large increases in nitrates due to calcium carbonate treatment. In soil 11077 the formation of nitrates was stimulated slightly by phosphate treatment.

Since mono-calcium phosphate stimulated nitrate formation in soil 11078 in pot tests, it was thought desirable to learn whether similar results would be obtained under field conditions. Accordingly small plots were prepared which received treatments of limestone, mono-calcium phosphate and mono-calcium phosphate plus limestone. The limestone was applied at the rate of 2 tons per acre and the phosphate at the rate of 200 pounds per acre.

In order to compare under similar conditions in the field the formation of nitrates in one of the soils that responds to lime treatment, sufficient fresh soil of number 11076 was obtained and beds 6 inches deep were prepared near soil 11078. One plot was left untreated while the other received an application of limestone at the rate of 2 tons per acre. Beginning April 1, samples were taken at intervals from the several plots and the nitrates determined. Table 7 reports the results obtained in parts per million of soil solution.

TABLE 6

The effect of phosphates upon nitrification

SOIL NUMBER	TREATMENT		NITRATES IN SOIL SOLUTION
	Material	Quantity	
		per cent	*p.p.m.*
11076	Control		316.0
11076	$CaCO_3$	0.25	380.0
11076	$CaH_4(PO_4)_2$	0.10	304.0
11076	$CaH_4(PO_4)_2$+$CaCO_3$	0.10 + 0.25	252.0
11076	$Ca_3(PO_4)_2$	0.15	276.0
11077	Control		152.0
11077	$CaCO_3$	0.10	144.0
11077	$CaH_4(PO_4)_2$	0.10	156.8
11077	$CaH_4(PO_4)_2$+$CaCO_4$	0.10+ 0.10	148.0
11077	$Ca_3(PO_4)_2$	0.15	144.0
11078	Control		178.0
11078	$CaCO_3$	0.25	168.0
11078	$CaH_4(PO_4)_2$	0.10	227.5
11078	$CaH_4(PO_4)_2$+$CaCO_3$	0.10+ 0.25	295.0
11078	$Ca_3(PO_4)_2$	0.15	160.0
11079	Control		66.8
11079	$CaCO_3$	0.56	118.0
11079	$CaH_4(PO_4)_2$	0.10	48.0
11079	$CaH_4(PO_4)_2$+$CaCO_3$	0.10+ 0.56	122.4
11079	$Ca_3(PO_4)_2$	0.15	60.0
11080	Control		7.2
11080	$CaCO_3$	0.70	72.8
11080	$CaH_4(PO_4)_2$	0.10	20.0
11080	$CaH_4(PO_4)_2$+$CaCO_3$	0.10+ 0.70	54.8
11080	$Ca_3(PO_4)_2$	0.15	12.0

TABLE 7

Nitrates formed in soils under field conditions

SOIL NUMBER	TREATMENT	NITRATES IN SOIL SOLUTION					
		April 1	April 15	April 23	May 2	May 9	May 22
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m*
11076	Control	Trace	11.2	18.4	32.5	4.9	14.1
11076	$CaCO_3$	Trace	16.3	26.0	43.2	8.0	24.1
11078	Control	Trace	4.8	8.4	13.2	2.8	6.0
11078	$CaCO_3$	Trace	5.1	9.2	14.1	2.6	6.2
11078	$CaH_4(PO_4)_2$	Trace	4.6	8.0	13.0	2.0	5.4
11078	$CaH_4(PO_4)_2$+$CaCO_3$	Trace	5.0	8.8	14.0	2.4	6.0

The development of nitrates under field conditions was similar to the pot experiments with respect to the calcium carbonate treatment but the influence of phosphates in the field tests did not confirm the results obtained in the pot tests. The inability to thoroughly mix the phosphate with the moist soil in the early spring may account for the failure to get the results anticipated. It is interesting to note that during the week between May 2 and May 9 there was a denitrification period that was consistent in all plots. At that particular time the weather was cold and somewhat wet which was probably conducive to denitrification. Attention is called to the comparative rapidity with which the nitrates formed in the two different soils treated with calcium carbonate. Both in the early spring and immediately following the denitrification period, soil 11076 formed large amounts of nitrates while soil 11078 acted much more slowly and gave but little increase due to the calcium carbonate treatment. When it is remembered that soil 11076 gives an increase in crop yields upon application of lime and that soil 11078 does not, it is evident that the rapid development of sufficient nitrates is an important influencing factor that may explain why one acid soil responds while another does not respond to lime treatment.

Work is being continued to ascertain why nitrates do not increase, as may be expected, in some acid soils after treatment with lime.

SUMMARY

A study has been made of the soil solution of five so-called "acid soils," three of which give increased crop yields from the application of lime while two do not.

Periodic determinations have been made of the water-soluble nutrients of these soils after treatment with $CaCO_3$, CaO and $CaSO_4$.

The main differential factor was the rapid development of a comparatively large amount of nitrates due to treatment with calcium carbonate or calcium oxide in those soils that respond to lime treatment while the other soils show much smaller increase in nitrates after similar treatment.

The water-soluble phosphorus and sulfur were very low in all soils and did not change appreciably due to the effects of the various treatments.

Treatment of all soils with calcium sulfate increased the water-soluble magnesium and potassium.

In pot experiments mono-calcium phosphate, and mono-calcium phosphate plus lime caused an increase in nitrates in those soils that do not show an increase to lime treatment alone. Field plot tests did not confirm these results.

Periodic determinations of nitrates in field plots showed that soil 11076, nitrifies rapidly when treated with limestone while soil 11077 showed very little increase.

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THE EFFECT OF LIME, LEACHING, FORM OF PHOSPHATE AND NITROGEN SALT ON PLANT AND SOIL ACIDITY, AND THE RELATION OF THESE TO THE FEEDING POWER OF THE PLANT.

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The study of the acidity of plant juices in relation to the supply of plant-food and the feeding power of the plant is a step in the direction of a clearer understanding of the relations of a plant to its environment. It is only recently that problems of this nature have been given any special attention. Hoagland (5) has carried on some studies on the relation of the nutrient solution to the composition and reaction of the cell sap of barley. Truog and Meacham (8) have reported some studies on the relation of soil acidity to the acidity of plant juices, and Clevenger (2) has studied some of the factors affecting the acidity of plant juices. The present investigation was undertaken to study the effect of limestone, leaching, form of phosphate and nitrogen salt on plant and soil acidity, and the relation of these to the feeding power of the plant.

EXPERIMENTAL

Plan of work

For this investigation, corn and soybeans were grown in quartz cultures with suitable nutrients. The corn cultures were grown by one of us in an investigation previously reported. For the details regarding the plan of these cultures the reader is referred to the previous paper (1). The general plan of the soybean cultures was quite similar. Some minor differences in the fertilizer treatments of the corn and the soybean are indicated in table 1.

Fifteen inoculated soybean seeds were planted in each 2-gallon pot and shortly thereafter thinned to the best 10 plants. The cotyledons were removed from the seedlings in order to hasten the appearance of differences in growth due to the various treatments. Each treatment was made in duplicate.

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TABLE 1

Weight, water content, and acidity of different parts of soy-bean plants, and acidity of soil extracts secured under treatments indicated

POT NUMBER	TREATMENTS*	WEIGHT				WATER AS PERCENTAGE OF GREEN WEIGHT		REACTION OF PLANT JUICE						REACTION OF SOIL EXTRACT
		Green		Air-Dry				Leaves	Stems and petioles	Roots			Nodules	
		Tops	Roots	Tops	Roots	Tops	Roots			Actual acidity	0.0684 *N* alkali added			
											1 cc	2 cc.		
		gm.	*gm.*	*gm.*	*gm.*	*per cent*	*per cent*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
105	None	19.6	38.4	3.6	2.3	81.6	94.0	6.17	6.07	6.36	8.12	8.58		7.43
107	Acid phosphate	90.8	62.9	17.2	4.4	81.0	93.0	5.82	5.50	6.33	8.36	9.59	6.31	8.00
109	Rock phosphate	36.3	46.4	7.4	2.9	79.6	93.8	5.99	6.21	6.58	8.27	8.69		8.15
111	Acid phosphate limestone (2 tons)	92.5	70.0	19.4	5.0	79.0	92.8	6.01	6.16	6.31	8.14	9.39	6.85	7.85
113	Rock phosphate limestone (2 tons)	32.1	43.3	6.4	3.0	79.9	93.1	6.38	6.48	6.31	8.31	8.98		8.31
115	Acid phosphate limestone (10 tons)	90.1	72.3	16 9	5.2	81.4	92.7	5.99	5.82	6.33	8.58	9.86		8.17
117	Rock phosphate limestone (10 tons)	28.9	45.0	5.4	3.4	80.7	92.4	6.61	6.21	6.42	8.07	8.61		8.43

* Rates of application on acre basis were: acid phosphate, 400 pounds; rock phosphate 2,000 pounds; and lime in the amounts indicated.

Just as they were beginning to open their flowers, the soybean plants were harvested. Their general appearance at this time is indicated in plate 1. Just before harvesting, the pots were leached with distilled water until 1 liter of drainage water was secured from each. These solutions were filtered immediately through Pasteur-Chamberland clay filters and determinations of the actual acidity were made. As the plants were harvested, portions were retained for dry-matter determinations.

The determinations of the acidity or hydrogen-ion concentration of the plant juices were carried out by the method previously described by one of us (3). Determinations were made on the leaves, the stems and petioles together, and the roots. The determinations were not made on the tops as a whole since it has been shown by one of us (4) that the reaction of the different parts may vary and that the proportion of leaves, petioles, and stems may thus be a factor influencing the values for the tops.

Growth and acidity of soybeans

The results from the soybean cultures are summarized in table 1 and shown graphically in figure 1. They clearly bring out the influence of an excess of carbonate on the availability of phosphates to the growing plant. The use of 2 tons of limestone with acid phosphate increased the yield over acid phosphate alone, in which case a lack of calcium carbonate probably prevented a more rapid plant growth. When 10 tons of limestone was used with acid phosphate there was a smaller yield than when no limestone was used. Here there was probably too much calcium carbonate present, which held up the availability of the phosphate to the plant. The production of roots increased with increased amounts of limestone, due possibly to increased activity, with lessening availability of the phosphate. In the case of the rock phosphate, increased amounts of limestone resulted in a smaller production of tops and a greater production of roots due to the increased difficulty of securing phosphorus. The lack of phosphorus was apparently reflected directly in the smaller production of tops; whereas the roots were stimulated to slightly greater activity. In every case the yields with acid phosphate were greater than those with rock phosphate.

Under the conditions indicated, the addition of calcium carbonate to the soil should be reflected in the reaction of the soil extract. The data show that this was the case. Although in every case the soil extract was alkaline, it was more alkaline when rock phosphate was used than when acid phosphate was used. Where rock phosphate was used, the greater the addition of limestone the more alkaline was the soil extract in all cases. Similarly with acid phosphate, the greatest alkalinity occurred when used with 10 tons of limestone, but strangely there was a less alkalinity when 2 tons of limestone was used than when none was used. This peculiar behavior of the soil extract was related to the growth of the plants in that the best growth was obtained with 2 tons of limestone. Evidently the more vigorous growing plants re-

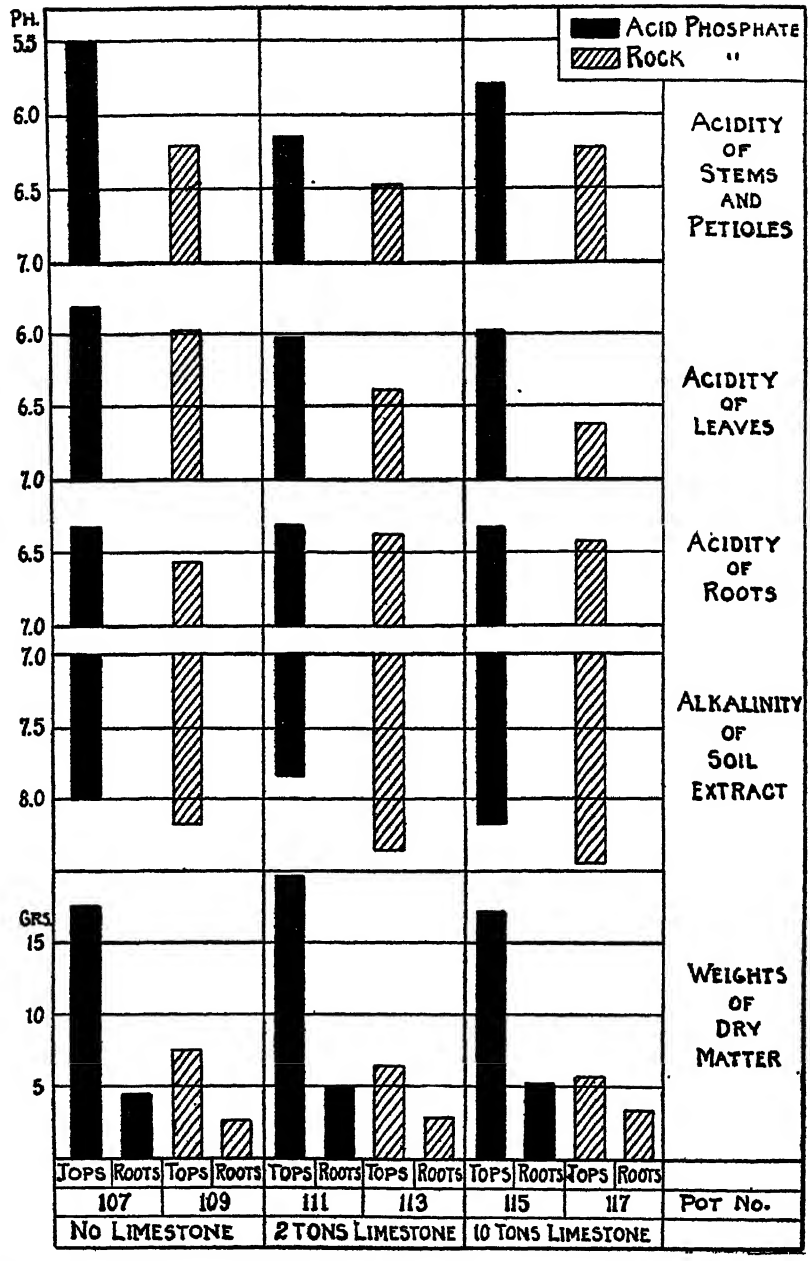

FIG. 1. DIAGRAM OF DATA FROM SOYBEAN CULTURES SHOWING EFFECT OF LIMESTONE AND FORM OF PHOSPHATE ON THE WEIGHT OF DRY MATTER AND REACTION OF THE PLANT JUICES AND SOIL EXTRACT

moved the soluble basic material more rapidly from the soil and thus brought about the decreased alkalinity.

With the increase of calcium carbonate, it might be expected that more of this compound would be assimilated by the growing plant, and as suggested by Truog (7), acids in the plant would be neutralized and precipitated. The data indicate that in general this was true. In every case the juices from the three parts of the plant were more acid when acid phosphate was used than when rock phosphate was used. The juice from the leaves in general was less acid with increased amounts of limestone, regardless of the form of phosphate. The juices of the other portions of the plants, however, did not show this regularity. With either form of phosphate the root juice was the most acid when 2 tons of limestone was used, which is the same relation as noted above for the acidity of the soil extract and the growth of the plants with acid phosphate, while the juice of the stems and petioles was least acid when 2 tons of limestone was used.

In addition to determining the actual acidity of the root juices, determinations were made also of the pH values of the juices after adding a definite amount of standard alkali to a given amount of juice. These data make possible comparisons as to the relative amount of acid in the plant juices. After 1 cc. of alkali was added, the root juice from plants grown in pots 109 and 117 with rock phosphate was less alkaline than the root juices from plants grown in pots 107 and 115 with acid phosphate; when 2 cc. was added the same relation still held. The root juice from the plants of pot 113 treated with rock phosphate and 2 tons of limestone was more alkaline than that of pot 111 treated with acid phosphate and 2 tons of limestone; when a total of 2 cc. of alkali was added this relation was reversed.

By means of the small hydrogen electrode vessel described by one of us (4), it was possible to determine the actual acidity of the juice of the soybean nodules. It was only possible to make these determinations on the nodules from two cultures; namely, those in which acid phosphate was used with no limestone, and with 2 tons of limestone. Without the use of limestone the actual acidity of the juice from the nodule protoplasm did not differ markedly from the actual acidity of the juice of the roots upon which the nodules grew. When 2 tons of limestone was used in addition to the acid phosphate, the juice of the nodule protoplasm became much less acid than the juice from the roots upon which the nodules grew. In this respect, the juice from the nodule protoplasm varied in about the same manner as the juices of the top portions of the plants.

Growth and acidity of corn

The dry matter yields and acidity determinations for the corn cultures are summarized in table 2 and shown graphically in figure 2.

The amount of dry matter produced varied widely with the different treatments. Leaching the cultures once a week always increased the yield when

TABLE 2

Weight of dry matter and acidity of the different parts of the corn plant and soil extract secured under the treatments indicated

POT NUMBER	TREATMENT*	DRY MATTER		REACTION OF PLANT JUICES									ACTUAL ACIDITY OF SOIL EXTRACT
				Leaves			Stalks			Roots			
				Actual acidity	Total acidity†		Actual acidity	Total acidity		Actual acidity	Total acidity		
		Tops	Roots		Litmus	Phenol-phthal-ein		Litmus	Phenol-phthal-ein		Litmus	Phenol-phthal-ein	
		gm.	*gm.*	*pH*	*cc.*	*cc.*	*pH*	*cc.*	*cc.*	*pH*	*cc*	*cc.*	*pH*
35	None	1.9	1.2										
37	Acid phosphate, $NaNO_3$, unleached	45.2	13.3	5.36	3.25	4.75	5.36	1.30	2.10	6.04	0.75	1.75	7.17
45	Acid phosphate, $NaNO_3$, leached	39.0	8.4	5.31	3.92	5.27	5.31	1.44	2.32	5.88	0.92	1.80	5.77
39	Rock phosphate, $NaNO_3$, unleached	18.3	6.2	5.36	3.80	5.17	5.67	1.17	2.03	6.02	0.29	0.93	8.18
47	Rock phosphate, $NaNO_3$, leached	23.4	6.9	5.31	4.32	5.92	5.62	1.37	2.32	5.87	0.57	1.37	6.70
41	Acid phosphate, NH_4NO_3, unleached	31.2	6.0	5.31	1.92	3.75	5.95	0.34	1.03	5.65	0.51	1.28	4.23
49	Acid phosphate, NH_4NO_3, leached	7.0	3.0	5.41	3.24	6.19	5.48			5.21	0.68	1.76	3.64
43	Rock phosphate, NH_4NO_3, unleached	38.8	8.2	5.49	1.92	3.98	5.60	0.80	2.37	5.64	0.51	1.24	4.74
51	Rock phosphate, NH_4NO_3, leached	58.9	10.5	5.45	3.10	5.71	5.58	0 98	2.35	5.48	0.96	2.60	4.46

* Rates of application on acre basis were: acid phosphate, 400 pounds; and rock phosphate, 2000 pounds.

† Total acidity expressed in terms of cubic centimeter of 0.0684 *N* NaOH.

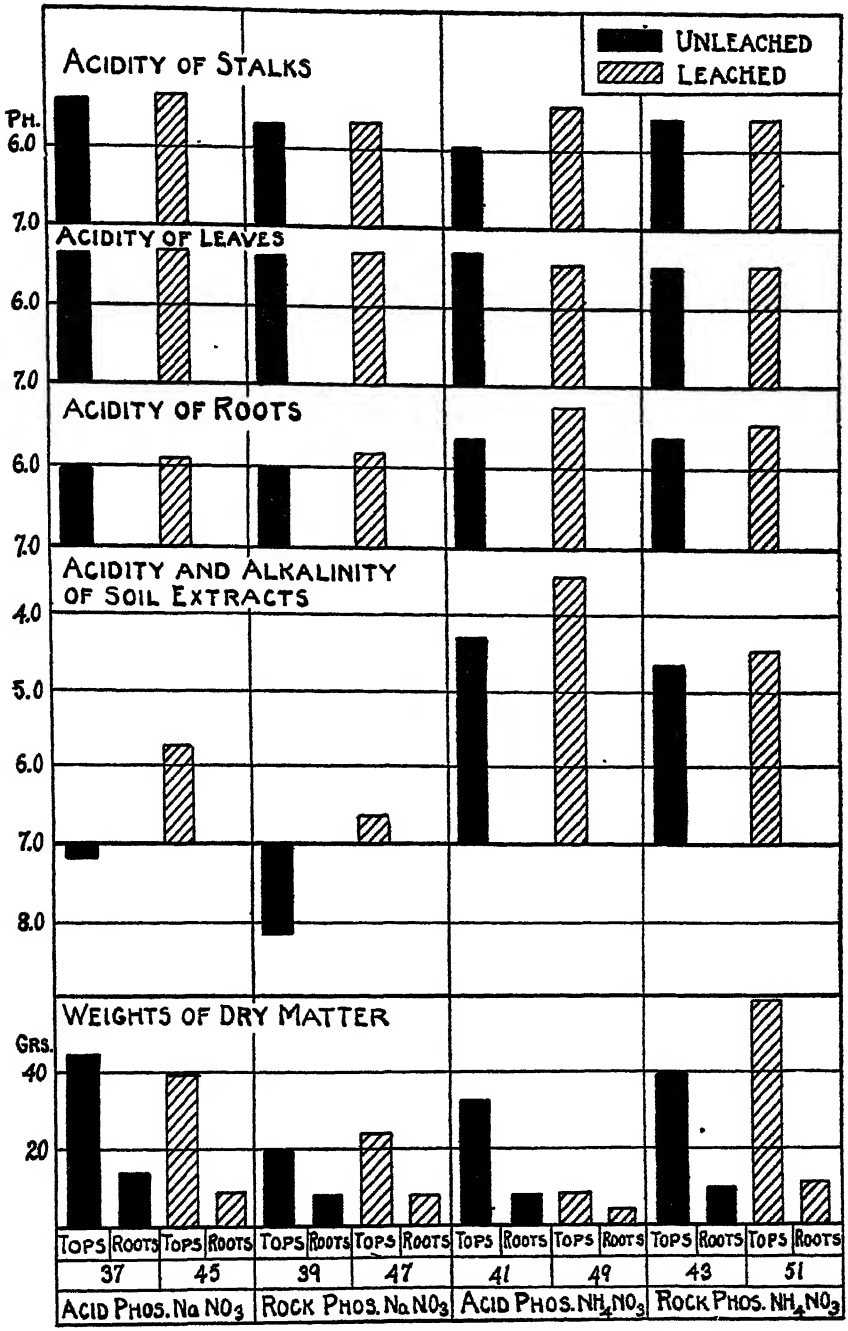

FIG. 2. DIAGRAM OF DATA FROM CORN CULTURE SHOWING THE EFFECT OF LEACHING, AND FORM OF NITROGEN SALT AND PHOSPHATE ON THE WEIGHT OF DRY MATTER AND REACTION OF THE PLANT JUICE AND SOIL EXTRACT

rock phosphate was used and decreased it when acid phosphate was used. This was evidently due to the removal of the soluble calcium salts. When rock phosphate was used the calcium salts were proportionately in excess of the soluble phosphate, with respect to the needs of the plant. Leaching removed these salts and thus permitted greater availability of the phosphate. When acid phosphate was used, leaching undoubtedly brought about a deficiency of calcium salts which was reflected in the retarded growth of the plants.

The question as to the possibility of leaching out sufficient soluble phosphorus where acid phosphate was used to limit plant growth, because of a deficiency of phosphorus, cannot be answered directly, since the leachings

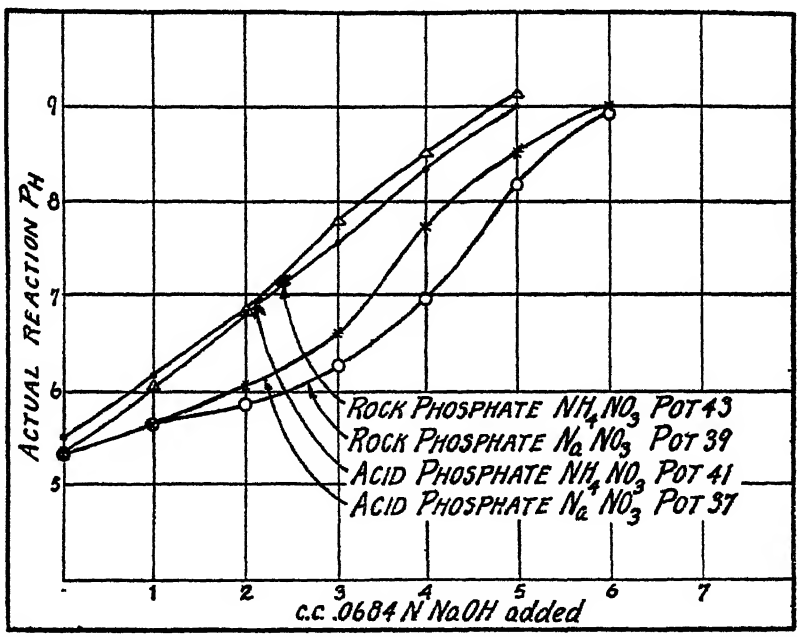

FIG. 3. CURVES SHOWING THE TOTAL ACIDITY OF THE JUICE OF CORN LEAVES AND SHEATHS GROWN IN UNLEACHED SOIL, IN TERMS OF CUBIC CENTIMETERS OF 0.0684 *N* NaOH

were not analyzed for phosphorus. It will be noted however, that, although leaching decreased the yield where acid phosphate and $NaNO_3$ were used, the yield from this culture was still among the best secured in the experiment.

When NH_4NO_3 replaced $NaNO_3$ as the source of nitrogen, the yields of dry matter were larger with rock phosphate than with acid phosphate. Leaching the soil increased this difference to the extent that the yields with acid phosphate became very small, while those with rock phosphate were the largest of any secured in the experiment. It is evident that NH_4NO_3 had a marked influence on the availability of the rock phosphate. This influence may have been due to one or more reasons; namely, its effect on the solubility of calcium

bicarbonate and its effect in increasing the acidity of the medium by becoming nitrified or acting as a physiologically acid salt.

The striking differences in plant growth due to the various treatments were accompanied with striking differences in the acidity of the soil extract. Leach-

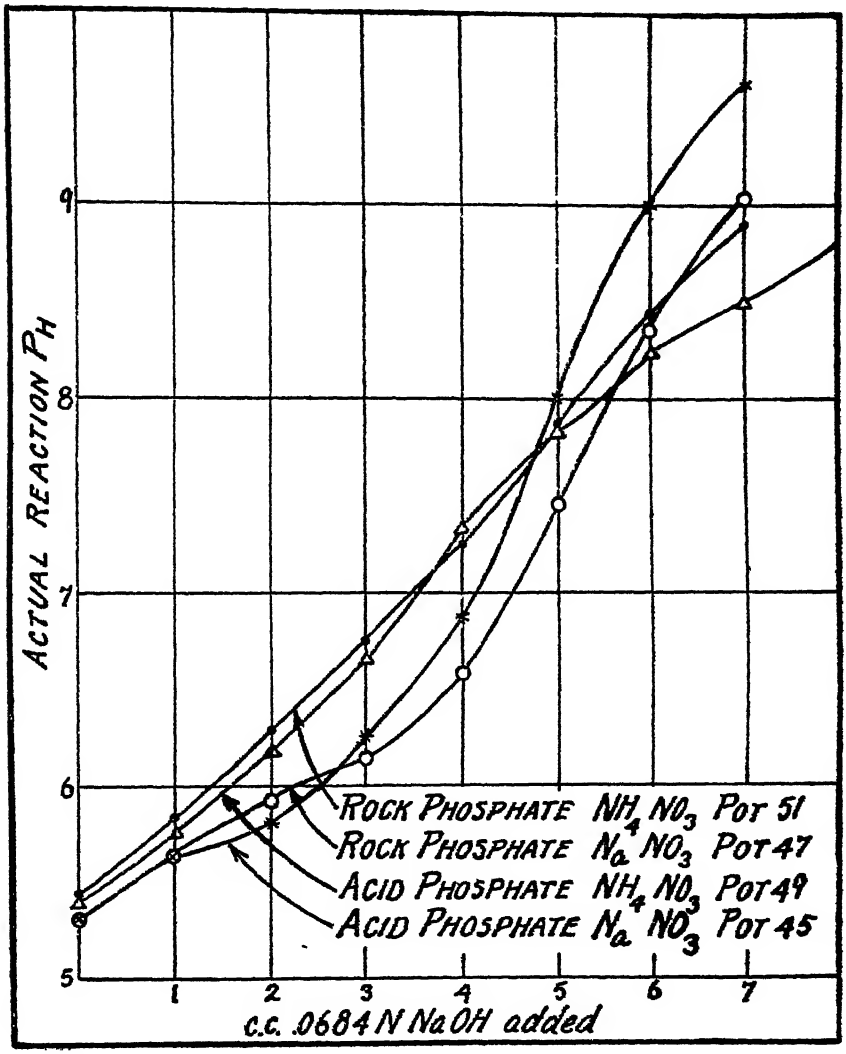

FIG. 4. CURVES SHOWING THE TOTAL ACIDITY OF THE JUICE OF CORN LEAVES IN LEACHED SOIL, IN TERMS OF CUBIC CENTIMETERS OF 0.0684 N NaOH

ing always increased this acidity and the greatest increase occurred when rock phosphate was used with $NaNO_3$. This increase in acidity readily explains why rock phosphate was made more available to corn by leaching. The soil extract was always more acid where acid phosphate was used in place of roc

phosphate. Ammonium nitrate always made the soil extract more acid than $NaNO_3$. The greatest difference in reaction of soil extract occurred between pot 39, treated with rock phosphate, but not leached, and pot 49, treated with acid phosphate and leached.

The yields of dry matter did not follow the acidity of the soil medium. The best growth did not take place under the most alkaline or the most acid conditions. The poorest yield of dry matter was produced where the greatest actual acidity, pH 3.64, prevailed which was with a combination of acid phosphate, NH_4NO_3, and leaching (pot 49). The next poorest yield was produced where the most alkaline condition, pH 8.18, prevailed, which was with a

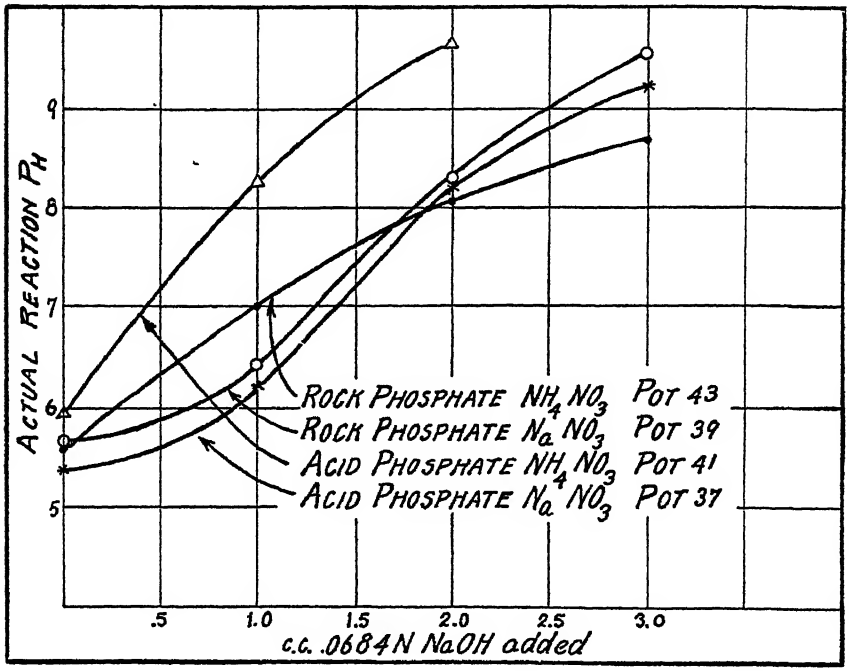

FIG. 5. CURVES SHOWING THE TOTAL ACIDITY OF THE JUICE OF CORN STALKS IN UNLEACHED SOIL IN TERMS OF CUBIC CENTIMETERS OF 0.0684 *N* NaOH

combination of rock phosphate, $NaNO_3$, and no leaching (pot 39). These two extremes of reaction were not suited for the best growth. The one produced such an acid reaction that physiological disturbances followed; the other so alkaline a reaction that the plant was unable to get sufficient phosphorus from the insoluble phosphate. Under the conditions of this experiment the best growth took place where the soil extract had a pH value of 4.46 (pot 51), and the next best where the pH value was 7.17 (pot 37). Evidently there is quite a wide range of acidity under which the plant may grow well, but the best conditions are well within the extremes made possible by fertilizer treatment.

The marked differences in the acidity of the soil were reflected in the acidity of the plant juice, though the variations in the plant were not so marked. In all cases except one, leaching caused greater acidity in the plant juice. The most striking differences due to leaching were found in the root and stalk

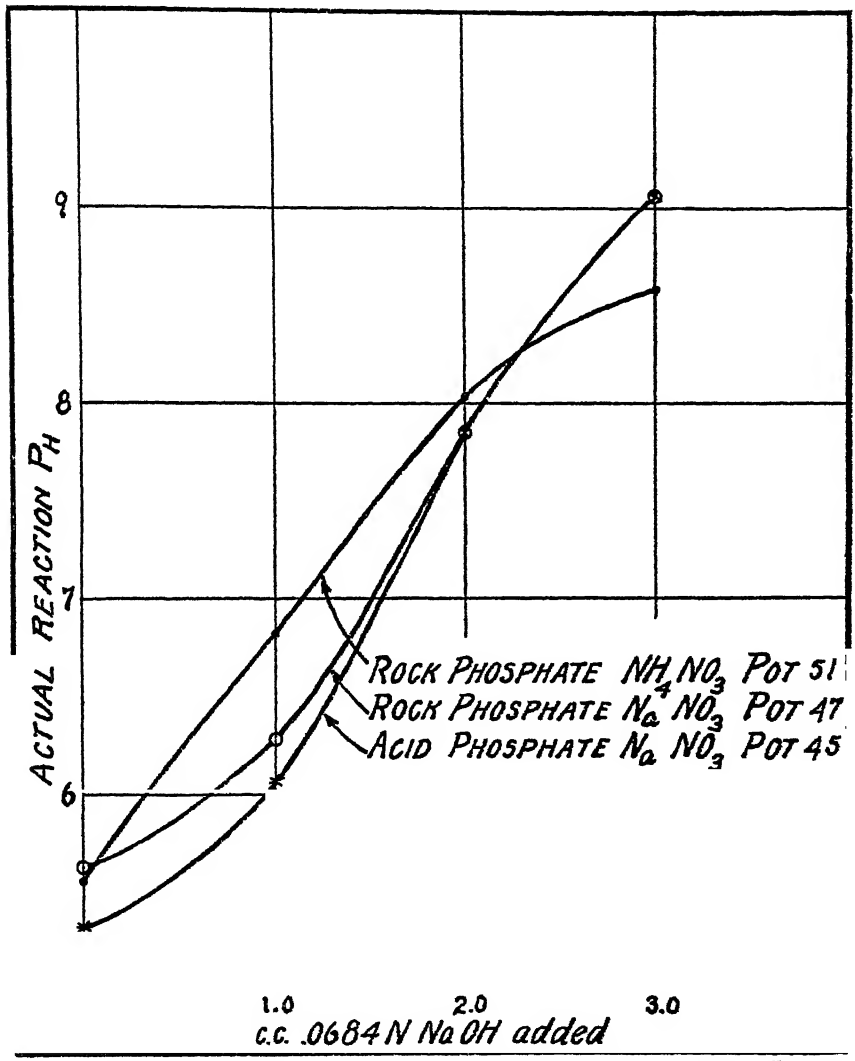

FIG. 6. CURVES SHOWING THE TOTAL ACIDITY OF THE JUICE OF CORN STALKS IN LEACHED SOIL, IN TERMS OF CUBIC CENTIMETERS OF 0.0684 *N* NaOH

juice of pots 41 and 49, treated with acid phosphate and NH_4NO_3. Neither acid phosphate nor rock phosphate influenced the acidity of the plant juices to a marked extent. In general, acid phosphate produced a slightly more acid condition in the plant. Ammonium nitrate as compared to $NaNO_3$, in-

creased the acidity of the root juice, but had little effect on the acidity of the tops, where in some cases there was even less acidity than with $NaNO_3$. In general the acidity of the root juice followed that of the soil, though the variations were not so wide as with the soil. The top portions of the plants were much more uniform in reaction, on account of the ability of these parts of the plants to counteract the acidity of environment by means of buffers and growth processes.

In table 2 are given the actual acidity and also the total acidity to litmus and phenolphthalein of the juices of the various parts of the corn plant. The pH values for the juices, after titrating with various quantities of standard

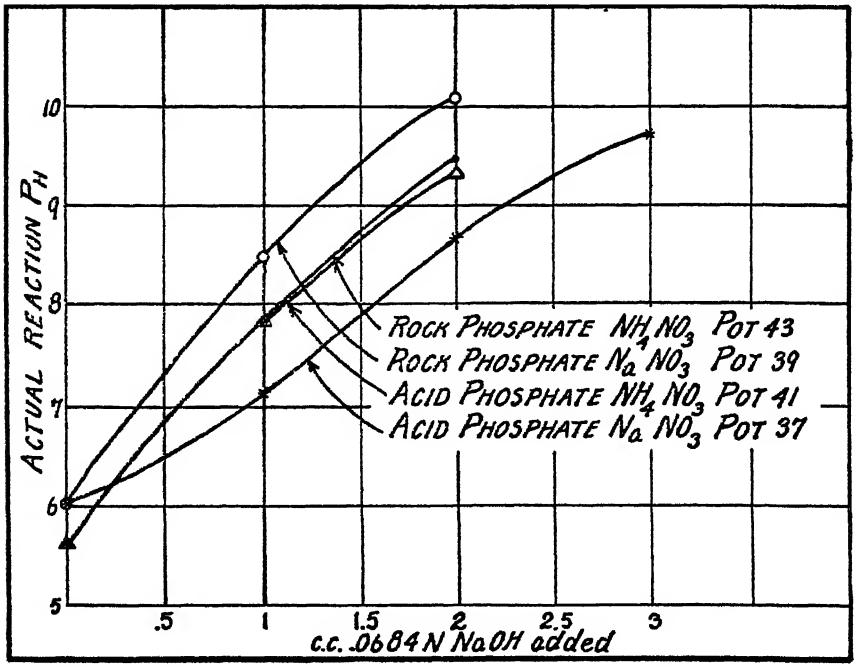

FIG. 7. CURVES SHOWING THE TOTAL ACIDITY OF THE JUICE OF CORN ROOTS IN UNLEACHED SOIL, IN TERMS OF CUBIC CENTIMETERS OF 0.0684 *N* NaOH

alkali, are given in tables 3, 4, and 5. The curves for these data are plotted in figures 3, 4, 5, 6, 7, and 8. The total acidity to litmus and phenolphthalein in terms of the standard alkali was secured from the curves. Litmus turns color at pH 6.81 and phenolphthalein at pH 8.3. Consequently, to determine the total acidity, according to these indicators it is only necessary to follow the ordinates to these points and from them the abscissae to the points where they are intercepted by the curve for any particular case. The length of the abscissa expressed in terms of cubic centimeters of 0.0684 *N* NaOH, is the value placed in table 2 for the total acidity to either litmus or phenolphthalein. Obviously from the curves, it is possible to secure the total acidity to any

indicator color change if it is known at what pH value the color change takes place.

The data for the total acidity of the juice of the corn plant follow the direction of those for the actual acidity. In 42 out of a total of 44 determina-

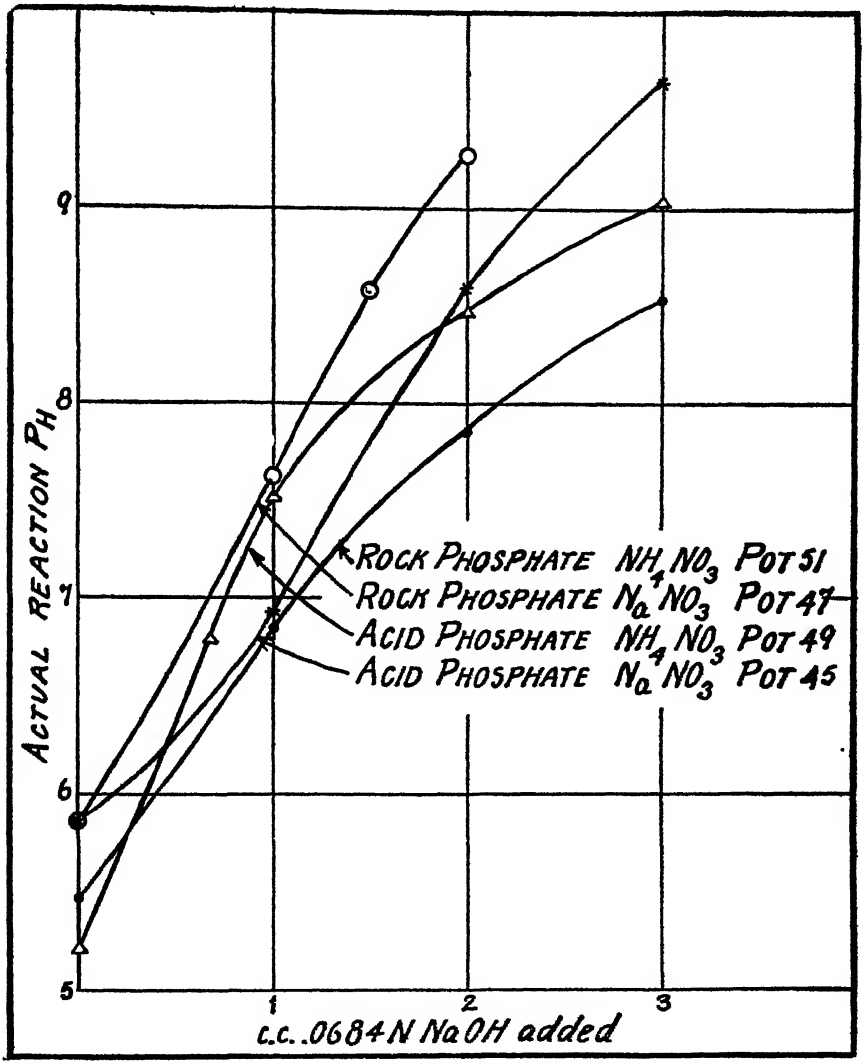

FIG. 8. CURVES SHOWING THE TOTAL ACIDITY OF THE JUICE OF CORN ROOTS IN LEACHED SOIL, IN TERMS OF CUBIC CENTIMETERS OF 0.0684 *N* NaOH

tions the total acidity was greater in the leached soil. It is also to be observed that the plant juice which had the greatest actual acidity also had the greatest total acidity. This is in accord with the results of Kappen (6) who found that as the actual acidity of the root juices of certain plants increased, the total

TABLE 3

The actual reaction in pH developed by the addition of standard alkali to the juice of the leaves and sheaths of corn plants grown under the conditions indicated. A volume of 10 cc. of juice, centrifuged 10 minutes, was used in each case.

0.0684 *N* NaOH ADDED	UNLEACHED CULTURES				LEACHED CULTURES			
	Acid phosphate $NaNO_3$ Pot 37	Rock phosphate $NaNO_3$ Pot 39	Acid phosphate NH_4NO_3 Pot 41	Rock phosphate NH_4NO_3 Pot 43	Acid phosphate $NaNO_3$ Pot 45	Rock phosphate $NaNO_3$ Pot 47	Acid phosphate NH_4NO_3 Pot 49	Rock phosphate NH_4NO_3 Pot 51
cc.	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
0.0	5.36	5.36	5.31	5.49	5.31	5.31	5.41	5.45
1.0	5.65	5.67	6.03	6.13	5.65	5.62	5.77	5.84
2.0	6.07	5.85	6.88	6.83	5.82	5.92	6.17	6.29
3.0	6.58	6.23	7.76	7.53	6.27	6.15	6.68	6.77
4.0	7.72	6.95	8.48	8.33	6.87	6.59	7.31	7.29
5.0	8.47	8.14	9.10	8.98	8.00	7.46	7.85	7.88
6.0	9.00	8.90			9.00	8.36	8.25	8.44
7.0					9.61	9.04	8.49	8.90
8.0							8.82	

TABLE 4

The actual reaction in pH developed by the addition of standard alkali to the juice of corn stalks grown under the conditions indicated. A volume of 10 cc. of juice centrifuged 10 minutes was used in each case.

0.0684 *N*. NaOH ADDED	UNLEACHED CULTURES				LEACHED CULTURES			
	Acid phosphate $NaNO_3$ Pot 37	Rock phosphate $NaNO_3$ Pot 39	Acid phosphate NH_4NO_3 Pot 41	Rock phosphate NH_4NO_3 Pot 43	Acid phosphate $NaNO_3$ Pot 45	Rock phosphate $NaNO_3$ Pot 47	Acid phosphate NH_4NO_3 Pot 49	Rock phosphate NH_4NO_3 Pot 51
cc.	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
0.0	5.36	5.67	5.95	5.60	5.31	5.62	5.48	5.58
1.0	6.21	6.41	8.25	7.02	6.06	6.29		6.83
2.0	8.19	8.29	9.64	8.04	7.85	7.85		8.04
3.0	9.20	9.56		8.69	9.07	9.04		8.58

TABLE 5

The actual reaction in pH developed by the addition of standard alkali to the juice of corn roots, grown under the conditions indicated, a volume of 10 cc. of juice, centrifuged 10 minutes, was used in each case.

0.0684 *N*. NaOH ADDED	UNLEACHED CULTURES				LEACHED CULTURES			
	Acid phosphate $NaNO_3$ Pot 37	Rock phosphate $NaNO_3$ Pot 39	Acid phosphate NH_4NO_3 Pot 41	Rock phosphate NH_4NO_3 Pot 43	Acid phosphate $NaNO_3$ Pot 45	Rock phosphate $NaNO_3$ Pot 47	Acid phosphate NH_4NO_3 Pot 49	Rock phosphate NH_4NO_3 Pot 51
cc.	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
0.0	6.04	6.02	5.65	5.64	5.88	5.87	5.21	5.48
1.0	7.10	8.47	7.83	7.82	6.92	7.61	7.51	6.87
1.5						8.58		
2.0	8.69	10.10	9.32	9.46	8.56	9.27	8.46	7.88
2.03							9.04	
3.0	9.71				9.64			8.53

acidity also increased. The data in table 2 indicate that not only does this hold true for the root juice of corn, but also for the juice of the leaves and stalks. In general the results also appear to confirm the findings of Kappen, namely, that the total acidity of the juice of the tops is greater than that of the roots. Further points of interest are the buffer effects indicated by the varied amounts of alkali required to bring the reaction of the juices from the litmus to the phenolphthalein color change, and the greater total acidity of the leaves and stalks when grown with $NaNO_3$ than with NH_4NO_3.

GENERAL DISCUSSION

The data presented in this paper show that lime, leaching, and the form of phosphate and nitrogen salt, had a marked effect on both the acidity of the quartz soil solution and of the plant juices, and that this acidity was closely related to the feeding powers of the plant. In accordance with the results obtained, these facts may be explained in the following manner.

Between the acids in the soil, or those present in local zones surrounding the feeding roots, and the rock phosphate and other salts, there was produced a condition of equilibrium. If the plant removed the soluble calcium salts along with the phosphates, the rock phosphate continued to go into solution. If, however, the calcium salts were not removed as rapidly as the phosphate, the soil became less acid and in consequence the rock phosphate was not so readily available. When limestone was used in addition to rock phosphate, the soil became still more alkaline and the phosphate still more unavailable. If, however, the soil was leached, the excess of calcium was removed, the soil became more acid and hence greater availability of the phosphate followed. If NH_4NO_3 was used in place of $NaNO_3$ as a source of nitrogen, still greater acidity appeared in the soil, and the rock phosphate also became still more available, even, indeed, surpassing the efficiency of acid phosphate in some cases.

The same explanation may also be given for the behavior of acid phosphate with the accompanying treatments. Here, however, on account of the more acid nature of acid phosphate, leaching and NH_4NO_3 intensified the deficiency of bases and the resulting acidity, which went to the point of practically preventing plant growth. On the other hand, it was possible to retard the availability of acid phosphate by the excessive use of limestone.

Of special interest in these experiments was the marked effect of NH_4NO_3 on the acidity of the soil medium. This may be explained by one or more of the following reasons: it may have acted as a physiologically acid salt, it may have produced acidity by becoming nitrified, and it may have directly increased the solubility and leaching of calcium bicarbonate. From the evidence previously reported (1), and from a study of the soil and plant acidity, it appears that the behavior of NH_4NO_3 as a physiologically acid salt is an important factor in relation to its effect in producing acidity of the soil medium. On the average, the top portions of the plants were less acid when grown with

NH_4NO_3 than with $NaNO_3$. The roots showed the reverse of this, partaking more of the nature of the reaction of the soil.

In the experiments with corn the actual acidity of the plant juices was directly affected by the acidity of the soil. In this respect the results are in accord with those of Truog and Meacham (8) which indicate that the acidity of the soil is usually directly reflected in the acidity of the plant juices. The total acidity of the juices varied in the same manner as the actual acidity, or hydrogen-ion concentration, which is the same relationship which Kappen (6) found to hold true for the juices of other plants. In the case of the soybean roots, while the hydrogen-ion concentration usually showed a direct relation to the acidity of the soil, the total acidity usually varied in the opposite direction. The explanation for this behavior of soybeans is not apparent.

The data of these experiments strikingly show the power possessed by plants to regulate internal acidity. Marked differences in the acidity of the soil caused only small differences in the acidity of the plant juices—the least variation was caused in the top portions of the plants, and the greatest variation in the roots. This would indicate that the roots are not so well provided with the means of counteracting the acidity as are the portions of the plant where the synthetic processes are taking place. The total acidity of the plant juices varied much more in this respect than the hydrogen ion concentration. These facts only serve to emphasize the power that the plant has in controlling the hydrogen-ion concentration in its juices, even though the total acidity changes considerably.

SUMMARY

The object of the experiments reported in this paper was to study the effect of leaching and certain fertilizer treatments on the acidity of the soil medium and plant juices, and to determine whether the acidity bore any relationship to the feeding power of the plant. For this purpose soybeans and corn were grown in quartz sand cultures which were variously treated with rock phosphate, acid phosphate, limestone, sodium nitrate, and ammonium nitrate. One series of the corn cultures was leached and the other was not. The acidity determinations of the plant juices included both the determination of the concentration of the hydrogen ions and the total acidity. The more important results of the investigations may be summarized as follows:

1. Ground limestone, leaching, and the form of phosphate and nitrogen salt had a marked effect on the acidity of the soil medium and plant juices. The acidity was closely related to the growth and feeding powers of the plants.

2. The use of ground limestone with soybeans increased the amounts of soluble calcium in the soil solution, and hence lessened the actual acidity of the soil and in general the actual acidity of the juices of the plant. In a few cases the limestone appeared to increase the vigor of growth which was accompanied by increased acidity of the plant juices.

3. Leaching the corn cultures removed soluble bases from the soil and hence increased the actual acidity of the soil, and usually also the actual acidity of the juices of the plant.

4. Acid phosphate always produced greater actual acidity or less alkalinity in the soil and usually greater actual acidity in the plant juices than did rock phosphate.

5. Greater actual acidity in the soil and plant juices caused a greater availability of rock phosphate to the plant.

6. Ammonium nitrate compared with sodium nitrate on corn had a marked influence in increasing the actual acidity of the soil and root juices, but an indifferent effect on the acidity of the top portions of the plant.

7. The total acidity of the roots of the soybean plant did not increase with increasing actual acidity. With the corn plant, however, the total acidity increased with the increase of actual acidity in the juices of both the tops and roots.

8. In general, the total acidity of the corn tops was greater than that of the roots.

9. The total acidity of the corn tops was usually greater when $NaNO_3$ was used than when NH_4NO_3 was used.

10. In the two determinations made, ground limestone appeared to lessen the actual acidity of the juice of soybean nodules to a greater extent than it did the actual acidity of the juice of the roots on which the nodules grew. The variation in the actual acidity of the juice of the soybean nodules due to liming was in the same direction as the variation in the actual acidity of the juices of the top portions of the plant.

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THE GROWTH OF SOYBEANS WITH TREATMENTS AS FOLLOWS:

Pot 105—No phosphorus.
Pot 107—Acid phosphate.
Pot 109—Rock phosphate.
Pot 111—Acid phosphate, 2 tons of limestone.
Pot 113—Rock phosphate, 2 tons of limestone.
Pot 115—Acid phosphate, 10 tons of limestone.
Pot 117—Rock phosphate, 10 tons of limestone.

INFLUENCE OF SALTS ON AZOFICATION IN SOIL

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INTRODUCTION

The influence of salts on ammonification (17) and nitrification (18) has been discussed in previous papers. It is the function of this paper to consider the action of the same compounds on azofication in the same soil as that used in the previous work. This was a loose calcarious soil, the physical and chemical analysis of which is given in table 1.

TABLE 1

Physical and Chemical Composition of Soil

PHYSICAL COMPOSITION			CHEMICAL COMPOSITION		
Grade		Per cent	Constituent		Per cent
Coarse sand	above 1 mm.....	17.69	Insoluble matter.....		66.69
Fine sand,	1 to 0.03 mm.....	37.39	Potash	(K_2O).....	0.55
Coarse silt,	0.03 to 0.01 mm....	15.19	Soda	(Na_2O).....	0.49
Medium silt,	0.01 to 0.003 mm...	10.36	Lime	(CaO).....	7.41
Fine silt,	003 to 0.001 mm....	10.32	Magnesia	(MgO).....	4.15
Clay	below .001 mm.....		Ferric oxide	(Fe_2O_3).....	2.93
Moisture and loss.....		9.05	Alumina	(Al_2O_3).....	3.49
			Phosphoric pentoxide	(P_2O_5)	0.25
			Sulphur trioxide	(SO_3).....	0.07
			Carbon dioxide	(CO_2).....	7.62
			Humus.....		2.18
			Total Nitrogen.....		0.15

The soil used, therefore, was a sandy loam very high in acid-soluble constituents, but the water-soluble constituents were not excessive. The calcium and magnesium contents were very high and mainly in the form of the carbonate. The soil was well supplied with phosphorus and potassium and there was a fairly large quantity of iron present. In fact all of the elements of plant-food were present in abundance, with the exception of nitrogen in which this soil was deficient. The soil was very productive and previous work had shown the ammonifying and nitrifying powers of the soil to be about the average for the soils of the arid regions. The nitrogen-fixing powers of the soil were above the average and previous work had shown it to have an intensely interesting bacterial flora.

PROCEDURE

Several hundred pounds of the soil were thoroughly mixed, stored in a large box, and kept as near field conditions as possible so that all the work could be done on the same soil. As the soil was needed in the work, portions were brought to the laboratory, air-dried in the dark, then weighed in 100-gm. portions into sterile covered tumblers. To each of these was added 1.5 gm. of lactose. The whole was then carefully mixed and the salt in most cases added from a carefully standardized stock solution. This, together with sufficient sterile distilled water to bring the moisture content up to 18 per cent, was thoroughly mixed in the soil. Each series, together with sterile blanks, was incubated at 28° to 30°C. for 21 days. Then nitrogen was determined by the Gunning (2) method, revised to include nitrates. In every case at least four determinations were made with each concentration of the salt, and, in the absence of agreement between determinations, the procedure for that series was repeated so that the results as herein reported are in every case the average of four or more closely agreeing determinations. Hence, experimental error has been reduced to as near a minimum as seemed to be possible in this kind of work.

The solutions of the salts were prepared by weighing gram-molecular quantities of Merck's best grade of the respective salts into 1000 cc. of sterile distilled water and then quantitatively determining the amount present. In those cases in which the analysis showed the concentration wrong, it was corrected, so that we have a definite knowledge of the quantity of salt added to the soil. The varying results reported by different investigators can in many cases, be attributed to the unknown variation in salts added. Solutions thus prepared were then added to the soil in such quantities that the anion and the cation can be directly compared the one with the other. The comparatively insoluble salts—calcium carbonate, calcium sulfate, etc.—were carefully weighed and intimately mixed with the soil. The arranging of the work in this order gives us as nearly absolute results as can be obtained by the present bacteriological methods, and at the same time gives us directly comparable results, which after all is what we have to look for in this work.

The salts tested were the chlorides, nitrates, sulfates, and carbonates of sodium, potassium, calcium, magnesium, manganese, and iron.

INFLUENCE OF SODIUM SALTS

In addition to the essential elements of plant-food applied to a soil, so-called soil amendments are often added. These may influence the physical, chemical, or bacterial properties of the soil. Some substances may alter the physical properties of the soil to such an extent that the bacterial flora is modified. Others may react chemically with constituents within the soil and in so doing liberate substances which can be utilized by the bacteria. Again, there may be a direct stimulation or retarding effect upon the organisms. Within this

field there is much yet to be learned concerning the nitrogen-fixing organisms. We have, however, some information concerning the influence of the so-called alkalies upon the nitrogen-fixing organisms.

A large number of analyses have shown that sodium salts are not necessary for the activity of *Azotobacter* (38) Lipman and Sharp (35) found no stimulation due to the common soil alkalies, sodium chloride, sodium sulfate, or sodium carbonate.

Azotobacter are, however, quite resistant to these compounds, as may be seen from the following report by Barnes and Ali (3):

Mgm. nitrogen fixed per gm. of mannite in nutritive solution inoculated with alkali soil	1.23
Mgm. nitrogen fixed per gm. of mannite in nutritive solution inoculated with sterile soil	7.80
Mgm. nitrogen fixed per gm. of mannite in nutritive solution inoculated with normal soil	7.07

Soil which contained sufficient salt to check all vegetation contained nitrogen-fixing organisms. Barnes and Ali hold that salts do not accumulate in the soil in sufficient quantities to kill the nitrogen-fixing organisms, but they are rendered inactive and as soon as the salts are leached from the soil the *Azotobacter* commence to work. Keutner (27) who worked with marine forms of the azofiers, found they would grow and assimilate nitrogen in an 8 per cent solution of sodium chloride. Nitrogen-fixers growing in arable soil would not be as resistant as are those which have become adapted to a medium with a high osmotic pressure, but *Azotobacter* in general appear to be more resistant to alkali salts than are most other soil organisms, for no toxic influence was noted by Lipman (35) until the concentration of sodium chloride in the soil reached 0.5 per cent, sodium sulfate 1.25 per cent, and sodium carbonate 0.4 per cent. They are much more sensitive to sodium in the form of nitrates, for 0.15 per cent stopped their multiplication and probably killed many of them (24). Remy (43) found sodium and potassium carbonate less favorable for nitrogen-fixation than were calcium or magnesium.

So far as the writer is aware, Krainskii (31) is the only worker who has found sodium carbonate more favorable than calcium carbonate. This may have been due to the liberation, by sodium carbonate, of plant-food which was in the soil in an insoluble form but which was essential to the development of *Azotobacter*. Mockeridge (38) has found that the presence of sodium salts is unnecessary and depressing at least to the growth of *Azotobacter*. The beneficial effect ascribed to sodium chloride solution in inoculating agar plates is due to the fact that this liquid is isotonic with the cell content solution, but the sodium hydroxide is a far less advantageous neutralizing agent than is calcium or magnesium carbonate.

The compounds used in this series were sodium chloride, sodium sulfate, sodium nitrate and sodium carbonate. They were used in concentrations 0 to 460 parts of sodium per million of soil. In each concentration the quantity of sodium in the various forms was constant.

The results are reported in table 2 in the form of percentages considering the nitrogen in the soil before incubation as 100 per cent. Each determination is the average of at least four and sometimes several times this number of closely agreeing determinations; hence the results should represent very closely the comparative influence of the various sodium salts upon azofication in this soil.

TABLE 2

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of sodium salts, after 21 days' incubation

QUANTITY OF SODIUM ADDED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION			
	Sodium chloride	Sodium sulfate	Sodium nitrate	Sodium carbonate
p.p.m.				
0.0	105.7	103.4	101.0	102.1
3.6	106.7	103.2	102.2	102.0
7.2	107.5	103.1	102.9	102 2
14.4	107.0	107.1	103.7	106.0
28.8	108.2	105.7	101.5	105.8
57.5	108 5	107.2	102.0	104.7
115.0	107.3	105.6	99.9	109.5
230.0	105.1	106.4	103.6	105.0
460.0	107.1	108.0	102.8	106.2

Each of the salts stimulate azofication at some concentration. This effect is most pronounced in the case of sodium carbonate and least in the case of sodium nitrate. It will be noted that this soil gained 9.5 per cent of nitrogen in the presence of 115 p.p.m. of sodium in the form of sodium carbonate whereas the same soil in the absence of sodium carbonate gained only 2.1 per cent. The chloride and sulfate also act as a strong stimulant. This is quite different from the results obtained by Lipman and Sharp (35). None of the salts become toxic at the concentrations used. Hence the nitrogen-fixing organisms, as maintained by Barnes and Ali (3), are considerably more resistant to soil alkalies than are the ammonifying or nitrifying organisms.

In this soil the various sodium salts became toxic to the ammonifying and nitrifying organisms at the following concentrations:

SALT	P P.M. OF SODIUM TOXIC TO:	
	Ammonifier	Nitrifiers
Sodium chloride	14.4	920.0
Sodium sulfate	23.8	7.2
Sodium nitrate	94.2	57.5
Sodium carbonate	2760.0	14.4

With the exception of sodium chloride then, these salts are even more toxic to the nitrifiers than they are to the ammonifiers

Moreover, sodium sulfate failed in every concentration to stimulate either the ammonifiers or nitrifiers whereas sodium carbonate failed in all concentrations to increase nitrification.

INFLUENCE OF POTASSIUM SALTS

Potassium is essential to the higher plants and cannot be replaced entirely by related substances, yet Gerlach and Vogel (14, 15, 16) early reached the conclusion that potassium and magnesium are not essential to the *Azotobacter*. Their results were, however, generally considered erroneous, for while as much nitrogen was fixed in 20 days without as with potassium after 40 days there was no further fixation in the solutions without potassium, but in its presence the nitrogen gain nearly doubled. It was, therefore, argued that the traces of potassium left in the chemicals and dissolved from the glass during sterilization had been enough to permit development for a time. If these elements are essential, it must be in extremely minute quantities, for Vogel (51) using the purest chemicals obtainable, was able to prepare potassium-free media in which the *Azotobacter* developed. He did find, however, that potassium favors their development.

The compounds used in the potassium series were the chloride, sulfate, nitrate and carbonate. The concentration varied from 0 to 782 parts per million of potassium. The results as reported in table 3 are the averages of four or more closely agreeing determinations.

TABLE 3

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of potassium salts

QUANTITY OF POTASSIUM APPLIED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION			
	Potassium chloride	Potassium sulfate	Potassium nitrate	Potassium carbonate
p.p.m.				
0.0	103.4	100.6	102.5	101.4
6.1	103.4	100.7	101.9	100.7
12.2	103.3	102.2	101.6	100.9
24.4	101.5	105.6	102.2	100.3
48.9	102.5	101.5	103.8	97.2
97.8	101.0	100.2	103.0	96.7
195.5	101.7	102.4	103.0	96.8
391.0	100.2	99.4	101.3	96.6
782.0	100.1	99.5	101.0	96.0

There is a marked difference between the sodium and potassium series. Although potassium is a nutrient it increased azoffcation only when applied to the soil as a sulfate whereas each of the sodium salts stimulated azofication. In this case, however, it must be borne in mind that we are dealing with a soil supplied with considerable available potassium. These data cannot, therefore, be taken to indicate that potassium is without effect upon nitrogen-fixing bacteria.

All except the nitrate of potassium became toxic at some concentration whereas none of the sodium salts became toxic in the concentrations used.

However, with the exception of potassium carbonate the potassium salts used are considerably more toxic to ammonifying and nitrifying organisms than they are to the azofiers.

INFLUENCE OF CALCIUM SALTS

The distribution and physiological efficiency of the nitrogen-fixing organisms, are governed by the physical and chemical properties of the soil, foremost among which is basicity, i.e., its content of calcium or magnesium carbonate (6). Ashby (1) bases his method for obtaining pure cultures of *Azotobacter* upon this property, for he finds that by picking out the crystals of the carbonate from the soil and seeding them into nitrogen-free media the likelihood of obtaining the organism is greatly increased. The addition of calcium carbonate to a soil often increases its azofying power (4). The extent of this increase depends on the lime requirements of the soil and on the fineness of the limestone added (30).

Christensen (7) has suggested that *Azotobacter* may be used as an index of the lime requirements of a soil. The test should include both a search for the organism in the soil and a test of their ability to grow when inoculated into the soil. He and Larson (8) examined more than one hundred soils of known lime requirement. They determined the carbon dioxide set free by acids, the amount of calcium dissolved by an ammonium chloride solution, the behavior of the soil toward litmus, and the biological test. The result of this test was that the biological test agreed with the known condition in 90 per cent of the cases, the ammonium chloride in 50 per cent, the litmus in 40 per cent, and the carbon dioxide failed more often than not to indicate the correct condition of the soil.

Fischer (12) failed to find *Azotobacter* in a heavy loam soil containing only 0.145 per cent of lime, while adjoining limed plots had an *Azotobacter* flora. The quantity of calcium carbonate which must be added to obtain maximum fixation varies with the soil (26).

A West Virginia Dekalb silt loam (7), which required 0.175 per cent of calcium carbonate to render it neutral by the Veitch method, gave greatest nitrogen fixation when 0.375 per cent of calcium carbonate was added. Above this concentration azofication decreased, but when phosphorus was applied with the lime it was not toxic even when present in quantities as great as 0.5 per cent. It is certain that large quantities of calcium carbonate may be present in soil without injury to the azofiers (38).

In many soils lime increases the amount of nitrogen fixed, for Krzemineniewski (33) found limed soil to fix 17.52 mgm. of nitrogen in 10 days, whereas adjoining unlimed soil fixed only 7.15 mgm. in the same time. There is, however, the possibility of applying too large a quantity of the caustic lime and thereby decreasing nitrogen-fixation (28), a condition which has never been experienced in the use of the carbonate.

Von Feilitzen (11), however, found neither a direct relationship between lime content of moor soil and the development of *Azotobacter*, nor a relationship between their development and the reaction of the soil. But this only serves to illustrate the fact that although lime and neutral or slightly alkaline media are essential, they will not insure a rich *Azotobacter* flora in a soil unless all other conditions are favorable.

Gainey (13) found that with a pH value of less than 6.0 there was no fixation of nitrogen in the soils studied by him.

Calcium carbonate and calcium oxide, in addition to furnishing a base which neutralizes the acid form in the metabolic processes of the *Azotobacter*, also furnishes calcium to the organism. Christensen (6) brought out the principle that *Azotobacter* can derive their calcium from dibasic calcium phosphate and some calcium salts of organic acids. They cannot, however, utilize the calcium of tribasic phosphate or of calcium chloride or sulfate.

The compounds which we used in the calcium series were the chloride, nitrate, carbonate and sulfate. The first two were added to the soil according to the usual method from a standard solution, whereas the carbonate and sulfate were weighed into the soil, carefully mixed, and then treated in the ordinary method.

A number of determinations were made in each case and compared with sterile blanks and the results reported in table 4 are the averages of four or more closely agreeing determinations.

Calcium chloride is the only one of the calcium salts which did not increase azofication. In the case of nitrate the increase is very pronounced, a concentration of 200 p.p.m. increased the nitrogen-fixing power ten times. The carbonate is slightly more efficient than the sulfate. It is interesting to note that we have here a soil with over 12 per cent of calcium carbonate and whose nitrogen-fixing powers is increased by the addition of calcium carbonate.

The addition of calcium chloride to this soil also stimulates ammonification but in high concentrations depresses nitrification, calcium sulfate acts in the same way on all three of the groups of organisms, ammonifiers, nitrifiers, and nitrogen fixers. Calcium nitrate, on the other hand, stimulates only the nitrogen fixers.

TABLE 4

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of calcium salts

AMOUNT OF CALCIUM ADDED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION			
	Calcium chloride	Calcium sulfate	Calcium nitrate	Calcium carbonate
p.p.m				
0	101.6	101.7	101.2	101.6
3	101.7	101.1	101.5	104.1
6	101.8	101.2	101.1	104.8
12	101.0	102.0	106.1	105.0
25	101.1	102.4	108.8	104.0
50	100.2	102.1	107.9	103.8
100	99.8	104.0	111.2	103.6
200	100.5	103.1	110.2	101.1
400	100.0	104.3	110.1	102.0

The chloride was the only salt used which became toxic to nitrogen fixers in the concentrations used whereas all except calcium carbonates at this concentration were toxic to ammonifiers and all but calcium chloride and sulfate were toxic to the nitrifiers. It, therefore, appears from these results that the azofiers in soil are considerable more resistant to calcium salts than are ammonifiers or nitrifiers.

INFLUENCE OF MAGNESIUM SALTS

The nitrogen-fixing organisms develop normally in the presence of either calcium or magnesium carbonate, but in liquid cultures the film develops earlier and contains less foreign organisms in the presence of magnesium carbonate than in the presence of calcium carbonate.

The actual nitrogen fixed, as reported by Ashby (1), is also greater where magnesium carbonate is used. This he attributes to the suppression of foreign organisms, by the magnesium, especially of the butyric acid ferments.

There is, however, a marked difference in the action of calcium carbonate and magnesium carbonate when they are applied in large quantities. Lipman and Burgess (34) found the calcium carbonate stimulating and never toxic to *Azotobacter chroococcum* in concentrations up to 2 per cent in mannite solution. The magnesium carbonate was sharply toxic in concentrations above 0.1 to 0.2 per cent in such cultures. The calcium salt is without effect when added to most soils up to 1.4 per cent, but the magnesium carbonate is even more toxic in soils than in solutions. Moreover, their work indicated that calcium exerts a protective influence, in both soils and solutions, against the toxic influence of magnesium. The best ratio of calcium to magnesium varies with solution and soil.

The compounds of magnesium used in this work were the chloride, carbonate, nitrate and sulfate. The results obtained are reported in table 5.

The nitrogen fixed in this series is low throughout but it shows an unmistakable stimulation in the case of the chloride, sulfate and nitrate. A point of toxicity was reached with the sulfate, nitrate, and carbonate.

TABLE 5

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of magnesium salts.

AMOUNT OF MAGNESIUM ADDED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION			
	Magnesium chloride	Magnesium sulfate	Magnesium nitrate	Magnesium carbonate
p.p.m.				
0.0	100.5	102.0	103.2	100.2
1.9	100.5	102.2	102.0	99.1
3.8	100.9	103.7	100.9	99.1
7.6	101.8	101.1	100.4	101.5
15.2	101.8	101.6	99.7	99.1
30.4	101.8	99.8	105.1	99.1
60.8	101.5	102.3	101.1	100.2
121.6	102.7	102.4	101.0	102.1
243.2	100.9	102.0	101.8	99.1

These results indicate that the organisms concerned in nitrogen fixation are more resistant to magnesium salts than are either the ammonifiers or nitrifiers.

INFLUENCE OF MANGANESE SALTS

Manganese is looked upon as one of the most active catalyzers, but the results obtained with it are not always concordant (41, 44).

Some experiments by Skinner and Sullivan (47) demonstrated the fact that manganese acts in various ways as a fertilizer. It is often without influence, occasionally injurious, but usually beneficial, its effect depending apparently upon the composition and character of the soil. The oxidation in soils under treatment with manganese salts was also studied and it was found that an increase in oxidation and growth frequently occurred in aqueous extracts of poor, unproductive soils; but while oxidation was increased in fertile soils, growth was decreased, the plans showing indications of excessive oxidation. Field experiments showed practically no effect from the manganese salts, but the soil was acid, a condition which may have accounted to a considerable degree for the nature of the results.

It is suggested that when the action of manganese is beneficial, it is probably due (a) to the increased oxidation produced in the plant roots whereby the plant is stimulated to greater activity and to increased absorption of the material useful for its growth and general metabolism; (b) to the stimulation of the activity of microörganisms in the soil; (c) to an increased oxidation within the soil.

The same authors suggest that when large applications of manganese have been found to be injurious, the injury is undoubtedly due to the "excessive stimulation and excessive oxidation in microörganisms and in the plant with a resulting change in the biochemical activities of plant and microörganisms and in the conditions of inorganic and organic soil constituents, the ultimate result of which change is injurious to the growing crop."

An Italian investigator (10) found that manganese carbonate added to the soil with a natural phosphocarbonate greatly increased the yield of wheat and alfalfa, whereas Pfeiffer and Blanck (41) found that manganese caused an increased assimilation of nutritive substances from the soil.

Although the addition of manganese to a soil often increases the nitrogen content of the crop (46) it does not increase the manganese content (22), thus indicating that its action is mainly on the biological transformation of nitrogen and possibly phosphorus which is going on in the soil.

TABLE 6

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of manganese salts

AMOUNT OF MANGANESE	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION			
	Manganous chloride	Manganous sulfate	Manganous nitrate	Manganous carbonate
p.p.m.				
0.0	101.4	101.0	100.8	101.3
4.3	102.1	103.4	98.6	100.4
8.6	102.7	98.6	98.1	101.3
17.2	103.7	98.6	99.3	100.3
34.4	102.9	98.5	100.2	100.1
68.8	102.3	101.5	98.6	100.3
137.6	100.7	101.6	98.0	100.9
275.2	100.8	101.2	103.0	101.3
550.4	100.9	98.8	102.9	100.4

While not essential to bacteria, manganese is an active catalyzer (20) in increasing proportions up to 6 mgm. per 100 cc. of media. Above this conncetration the reaction falls off rapidly and at 20 mgm. it is less than in the absence of manganese. It is oxidized by *Azotobacter*, and in the proportions of 1 to 200,000 parts of soil it is an active stimulant. Olaru (39) considers it likely that the increased yield obtained after the application of manganese compounds to a soil is due to its accelerating the action of the nitrogen-fixing organisms. He found that in the right concentration manganese has a very favorable influence upon *Azotobacter chroococcum* (40). The results obtained in our experiments with manganese are given in table 6.

The chloride and nitrate are the only ones which stimulate the azofiers and in the case of these it is very weak as compared with the action of manganese upon the ammonifiers and nitrifiers which in appropriate concentrations is very pronounced. These results indicate that the beneficial results from the use of manganese is due mainly to their influence upon the ammonifiers and nitrifiers and not the nitrogen fixers. Hence they would have to be

classed as mere soil stimulants which do not increase the total soil fertility but render more available some constituents which are probably, the nitrogen, phosphorus and potassium (19). However, the toxicity of the manganese compounds are not so great for the azofiers as they are for the ammonifiers and nitrifiers.

INFLUENCE OF IRON SALTS

Iron (28) is essential to the nitrogen-fixing microörganism, and either the ferric or ferrous sulfate is especially beneficial (29). Rosing (45) found the amount of nitrogen fixed increased from 2.23 mgm. to 10.3 mgm. per gram of mannite when iron sulfate was added to the cultural media. This is due, in a great degree, to the iron which serves as food for the organism, yet its colloidal nature may play a part, for both organic and inorganic colloidal substances have an especially favorable action on *Azotobacter* although the action of the inorganic colloids is fully manifest only in the presence of organic colloids (42). If used alone, large quantities of the ferric hydroxide are essential for the maximum effect, but in the presence of organic colloids, very small quantities of iron are effective. This has been attributed to the action

TABLE 7

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of iron salts

AMOUNT OF IRON ADDED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION			
	Ferric chloride	Ferric sulfate	Ferric nitrate	Ferric carbonate
p.p m.				
0.0	102.4	102.5	106.7	101.4
2.9	100.8	102.6	108.7	102.7
5.8	101.5	102.5	106.3	101.8
11.6	103.3	102.9	106.8	103.2
23.2	103.3	102.1	108.0	101.0
46.5	103.3	101.6	105.9	100.0
93.0	104.2	101.7	107.3	99.4
186.0	104.2	100.4	106.7	100.0
372.3	106.8	101.1	95.5	100.2

of the colloidal iron which absorbs the nitrogen and oxygen of the air and brings them into more intimate contact with the *Azotobacter* (48). This would not only accelerate the normal processes of the aerobic *Azotobacter* by furnishing them with nitrogen and oxygen but it would tend to suppress the anaerobic processes which are extremely wasteful of the food.

The compounds used in this series were ferric chloride, ferric sulfate, ferric nitrate and ferrous carbonate. All except the carbonate were added to the soil in solution. The carbonate was added in the form of a dry powder and carefully mixed with the soil. Considerable difficulty was experienced in obtaining duplicate determinations to agree when the sulfate was applied to the soil and the results as reported for sulfate represent the average of eight sets of determinations. The chloride, nitrate, and carbonate represent the average of four closely agreeing sets of determinations. The results are given in table 7.

All of the iron compounds stimulated nitrogen fixation. The stimulation is most pronounced in the case of the chloride and least in the case of the sul-

fate. The influence upon this group of organisms is not nearly so pronounced as the influence of iron salts on ammonifying and nitrifying microörganisms. The stimulation of the three groups of soil organisms together with results obtained when higher plants are treated with iron salts (19) make it certain that the increased yield obtained from the use of iron salts is due in a very marked degree to the action of these compounds upon soil microörganisms.

INFLUENCE OF CHLORIDES

So far in this discussion we have been comparing the action of compounds having the same electro-positive ion but various electro-negative ions. Hence, the results considered have given us an insight into the influence of the anions Cl, SO_4, NO_3, and CO_3, upon the nitrifying efficiency of the soil. It is therefore interesting to compare the compounds which have a constant anion and various cations. This is done in table 8. In this series we have the chlorides of sodium, potassium, magnesium, calcium, manganese, and iron. The experiment was so arranged that equivalent quantities of chlorine in the various forms were applied to 100 gm. of soil. Each reported result is the average of four or more closely agreeing determinations.

TABLE 8

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of chlorids

AMOUNT OF CHLORIDE	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION					
	Sodium chloride	Potassium chloride	Calcium chloride	Magnesium chloride	Manganous chloride	Ferric chloride
p.p.m.						
0.0	105.7	103.4	101.6	100.5	101.4	102.4
5.54	106.7	103.4	101.7	100.5	102.1	100.8
11.08	107.5	103.3	101.8	100.7	102.7	101.5
22.16	107.0	101.5	101.0	101.8	103.7	103.3
44.32	108.2	102.5	101.1	101.8	102.9	103.3
88.65	108.5	101.0	100.2	101.8	102 3	103.3
177.30	107.3	101.7	99.8	101.5	100.7	104.2
354.60	105.1	100.2	100.5	102.7	100.8	104.2
709.20	107.1	100.1	100.0	100.9	100.9	106.8

It is evident that all of the chlorides with the exception of calcium chloride and possibly potassium chloride stimulate the azofiers of the soil. This is not due alone to the electro-negative ion for the extent of stimulation varies widely with the anion. It is very pronounced where ferric chloride has been applied to the soil and is barely perceptible where potassium chloride has been used. Moreover, the concentration at which maximum stimulation occurs varies with the specific salt. These concentrations are as follows:

Salt	*parts of Cl per million of soil mixture*
Sodium chloride	44
Calcium chloride	11
Magnesium chloride	354
Manganous chloride	22
Ferric chloride	709

Three of the compounds—potassium, calcium and manganous chloride became toxic at the concentrations tested whereas the others did not.

The results as a whole, however, bears out the conclusion that the benefical effect of the chlorides were due in no small measure to their action upon soil microörganism which in turn render more plant food available.

INFLUENCE OF SULFATES

The results obtained with the various sulfates are summarized in table 9.

TABLE 9

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of sulfates

AMOUNT OF SULFATE	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION					
	Sodium sulfate	Potassium sulfate	Calcium sulfate	Magnesium sulfate	Manganous sulfate	Ferric sulfate
p.p.m.						
0.0	103.4	100.6	101.7	102.0	101.0	102.5
7.5	103.2	100.7	101.1	102.2	103.4	102.6
15.0	103.1	102.2	101.2	103.7	98.6	102.5
30.0	107.1	105.6	102.0	101.1	98.6	102.9
60.0	105.7	101.5	102.4	101 6	98.5	102.1
120.1	107.2	100.2	102.1	99.8	101.5	101.6
240.2	105.6	102.4	104.0	102.3	101.6	101.7
480.3	106.4	99 4	103.1	102.4	101.2	100.4
960.6	108.0	99.5	104.3	102.0	98.8	101.1

Magnesium sulfate and ferric sulfate fail to stimulate azofication in any of the concentrations tested. All of the other sulfates have a pronounced stimulating influence at some concentration. At a concentration of 960.6 parts of sulfate per million of soil mixture the total nitrogen of the soil was increased 2.6 per cent in the case of calcium sulfate, 4.6 per cent in the case of sulfate of sodium and 5 per cent in the case of potassium sulfate. These compounds may, therefore, actually increase the soil fertility aside from the sulfur and potassium carried. Moreover, the sodium and calcium sulfate can be looked upon other than as stimulants, for in addition to the phosphorus, potassium and nitrogen which they render available they also increase the total nitrogen supply of the soil through their action upon the azofiers.

Potassium sulfate acts quite differently from the sodium in that the former became toxic in the higher concentrations whereas the latter did not. This same phenomenon appeared in the ammonifying and nitrifying tests when potassium sulfate was considerable more toxic than sodium sulfate. However, the resistance of the azofiers is greater to these salts than are the other classes of microörganisms. Ferric sulfate also becomes toxic but at a concentration much greater than that at which it becomes toxic to other soil organisms. It appears probable that the beneficial action of these various salts towards azofiers may be due in a measure to their suppressing of other species which compete with the azofiers for the limited supply of organic carbon in the soil.

INFLUENCE OF NITRATES

A marked difference between the azofiers and higher plants and other bacteria is that they possess the power of obtaining their nitrogen from the air, but in the presence of combined nitrogen they obtain but little from the air (50). Lipman (36), Stranak (50), Heinze (23), and Stoklasa (49) found that small quantities of nitrates stimulated *Azotobacter*, whereas large quantities discourage nitrogen-fixation since the organisms live on the nitrates. This is the case whether the nitrates are added to the soil or to the solution in which nitrogen-fixation is taking place. Coleman (9) considers this action as due to several different factors, namely, (a) a direct toxic action of the salt, (b) antagonism of other organisms which it favors, (c) the using up of the energy supply by these organisms, and (d) the discouragement of fixation by the use of sodium nitrate. The last would seem to be the most important factor when viewed in connection with the following results reported by Hills (21):

TREATMENT NITRATE	RELATIVE NUMBER* OF ORGANISMS			RELATIVE PER CENT OF NITROGEN FIXED			
				Sterilized soil		Unsterilized soil	
	KNO_3	$NaNO_3$	$Ca(NO_3)2$	$NaNO_3$	$Ca(NO_3)2$	$NaNO_3$	$Ca(NO_3)2$
mgm							
0	100	100	100	100	100	100	100
10	348	191	362	100	105	240	219
50	8,210	3,150	4,528	342	371	500	444
150	12	117	763				
200	0	0	0	352	467	879	557

* The number of organisms developing and nitrogen fixed in the one receiving no nitrate is taken as 100 per cent.

It is quite evident from these results that although nitrates cause more active multiplications of *Azotobacter*, it greatly reduces their physiological efficiency. The organisms used by Hills had probably grown for a long time on media poor in nitrogen, and their ability to fix nitrogen was, therefore, high, But would they continue to exert this power if grown on media rich in nitrogen? The evidence points strongly to the conclusion that they would not.

Bonazzi (5) even argues from a recalculation of Hills results where he used *Azotobacter chroococcum* in synthetic media that nitrates either in the form of sodium nitrate or ammonium nitrate cause a very appreciable loss of nitrogen either as free nitrogen or as a volatile nitrogenous compound. He further considers it probable that whereas *Azotobacter chroococcum* may be a fixer of atmospheric nitrogen under such conditions as we may call "normal." i.e., is the absence of fixed nitrogen and a denitrifer when such conditions are changed so it may feed upon nitrates.

Nitrates and ammonium sulfate are rather effective in stimulating nitrogen-fixation when the *Azotobacter* are grown in connection with the cellulose ferments (37). Even here, however, large quantities have been found to decrease this power. In pure cultures ammonium sulfate (32, 36) seriously retards nitrogen-fixation, whereas the nitrogen of humus, even in large quantities, appears to have no serious retarding influence. Nevertheless, a high nitrogen content of soil seems to be unfavorable to a vigorous nitrogen-fixation whether this would be the case where the nitrate content of the soil is kept low but the readily decomposable nitrogen high, is yet to be answered. Hiltner and Stormer (25) consider that when the nitrogen content of the soil passes beyond a certain limit, the decay bacteria increase rapidly, and in the struggle for existence they are able to suppress the more slowly growing *Azotobacter*. This latter contention would not seem to be borne out by our results for we find that the nitrates become toxic to the ammonifiers and usually to the nitrifiers before they were toxic to the azofiers.

The compounds used in this series were sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate, manganous nitrate, and ferric nitrate.

TABLE 10

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of nitrate salts

AMOUNT OF NITRATE ADDED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION					
	Sodium nitrate	Potassium nitrate	Manganous nitrate	Calcium nitrate	Magnesium nitrate	Ferric nitrate
p.p.m.						
0.0	101.0	102.5	100.8	101.2	103.2	106.7
9.7	102.2	101.9	99.6	101.5	102.0	108.7
19.4	102.9	101.6	98.1	101.1	100.9	106.3
38.8	103.7	102.2	99.3	106.1	100.4	106.8
77.6	101.5	103.8	100.2	108.8	99.7	108.0
155.2	102.0	103.0	98.6	107.9	105.1	105.9
310.4	99.9	103.0	98.0	111.2	101.1	107.3
620.8	103.6	101.0	103.0	110.2	101.0	106.7
1,241.6	100.8	101.0	102.9	110.1	101.8	95.5

The quantity added to the soil was such that in each case equivalent quantities of nitrate in the various forms were added to the soil. Hence, the varying factor is the electro-positive ion, and the electro-negative remained the same in each case. The results are given in table 10.

There is an unmistakable fixation of nitrogen in each of these soils in the presence of nitrates. This fixation is even greater in the presence of the nitrate and lactose than it is in the presence of lactose alone. Thus showing that small quantities of nitrates in a soil stimulate nitrogen fixation. The calcium salt is considerably more efficient than are the sodium or potassium salts. The total quantity of nitrogen in this soil was only 0.15 per cent. But the addition of 2 per cent of dried blood plus the various forms of nitric nitrogen stimulated fixation to even a greater extent as may be seen by the results given in table 11.

Sodium nitrate-treated soil shows only a small gain in nitrogen, whereas potassium nitrate-treated soil shows an actual loss. But in the presence of calcium, magnesium or iron nitrate there was a fixation of four to eight times that actually fixed in the untreated soil.

Every one of these soils showed a loss of nitrates at the end of the incubation period but it had been transformed into protein nitrogen and not lost as has been interpreted by some workers. Moreover, these results make it clear that the azofiers in the soil are injured sooner by the potassium and sodium nitrate than by other forms of nitric nitrogen. These results are quite different from those obtained in solutions where the areation would not be favorable for nitrogen fixation. But the results indicate that in a normal calcareous

TABLE 11

Quantity of nitrogen obtained from 100 gm. of soil receiving various treatments

TREATMENT	NITROGEN IN 100 GM OF SOIL	EXCESS IN NITRATE TREATED SOIL	GAIN OR LOSS IN NITROGEN OVER SOIL RECEIVING NO NITRATE
	mgm	*mgm*	*mgm*
Dried blood, no nitrate	333.9		
Dried blood 84.06 mgm. of nitrogen as sodium nitrate	419.3	85.4	1.34
Dried blood, 84.06 mgm. of nitric nitrogen as calcium nitrate	460.5	126.6	42.54
Dried blood, 84.06 mgm. of nitric nitrogen as ferric nitrate	455.0	121.1	37.04
Dried blood, 84.06 mgm. of nitric nitrogen as magnesium nitrate	466.5	132.6	48.54
Dried blood, 84.06 mgm. of nitric nitrogen as manganous nitrate	443.1	109.2	25.14
Dried blood, 84.06 mgm. of nitric nitrogen as potassium nitrate	412.0	78.1	− 5.96

soil the losses from dentrification on the application of reasonable quantities of nitrate is zero. Moreover, in place of retarding beneficial bacterial activities nitrates actually increases them.

INFLUENCE OF CARBONATES

The compounds used in this series were the carbonates of sodium, potassium, calcium, magnesium, manganese and iron. The results are given in table 12.

Sodium, calcium and ferric carbonate are pronounced stimulants of the azofiers whereas potassium, magnesium and manganous carbonate are without effect. This effect is quite different from that upon the ammonifiers which were stimulated by all of the carbonates. Sodium, potassium, or calcium carbonates did not stimulate the nitrifiers in this soil.

Potassium, magnesium and ferric carbonate became toxic at some of the concentrations used but at higher concentrations than at which they became toxic to the other groups of organisms.

TABLE 12

Percentages indicating nitrogen fixed in 100 gm. of soil containing 1.5 gm. of finely powdered lactose and varying amounts and forms of carbonates

AMOUNT OF CARBONATE ADDED	PERCENTAGE OF INITIAL NITROGEN IN SOIL AFTER INCUBATION					
	Sodium carbonate	Potassium carbonate	Calcium carbonate	Magnesium carbonate	Manganous carbonate	Ferric carbonate
p.p.m.						
0.0	102.2	101.4	101.6	100.2	101.3	101.4
4.7	102.0	100.7	104.1	99.1	100.4	102.7
9.4	102.2	100.9	104.8	99.1	101.3	101.8
18.7	106 0	100.3	105 0	101.5	100 3	103.2
37.5	105.8	97.2	104.0	99.1	100.1	101.0
75.0	104.7	96.7	103.8	99.1	100.3	100.0
150.0	109.5	96.8	103.6	100.2	100.9	99.4
300.0	105.0	96.6	101.1	102.1	101.3	100.3
600.0	106.2	96.0	102.0	99.1	100 4	99.3

SUMMARY

The toxicity of the chlorides, nitrates, sulfates and carbonates of sodium, potassium, calcium, magnesium, manganese and iron as determined by nitrogen fixation is governed by the specific salt and not by the electronegative ion, as was the case with the ammonifers. In this regards the azofiers are similar to the nitrifiers.

These salts are all less toxic to azofiers in the soil tested than they are to the ammonifers or nitrifers.

The quantity of a salt which can be applied to a soil without decreasing the nitrogen gains varies with the salt. None of the sodium salts were toxic when 460 p.p.m. of sodium in the form of the various salt was applied to the soil. Calcium nitrate, sulfate and carbonate at 400 p.p.m., magnesium chloride and sulfate at 243 p.p.m., manganous nitrate at 550 p.p.m and ferric chloride at 372 p.p.m., were not toxic. The remaining salts became toxic at some concentration tested, in the following order:

1. $MgCO_3$
2. $Mg(NO_3)_2$
3. K_2CO_3
4. $FeCO_3$
5. $MnCO_3$
6. $Fe(NO_3)_3$
7. $Fe_2(SO_4)_3$
8. $CaCl_2$
9. $MnCl_2$
10. KCl
11. K_2SO_4
12. KNO_3
13. $MnSO_4$

KCl, K_2CO_3, $MnCO_3$ and $Fe_2(SO_4)_3$ failed to stimulate the nitrogen-fixing organisms in any of the concentrations tested. All the others stimulated the organisms in the following order:

1. $Ca(NO_3)_2$	6. $CaCO_3$	11. $MnCl_2$	16. $MgCO_3$
2. Na_2CO_3	7. NaCl	12. $Mn(NO_3)_2$	17. $FeCO_3$
3. K_2SO_4	8. $NaNO_3$	13. $MgCl_2$	18. $MgSO_4$
4. Na_2SO_4	9. $MnSO_4$	14. $Fe(NO_3)_3$	19. KNO_3
5. $FeCl_3$	10. $CaSO_4$	15. $Mg(NO_3)_2$	20. $CaCl_2$

The common soil alkalies would have to be present in soil in sufficient quantities to greatly retard ammonification, nitrification and plant growth before they would retard nitrogen fixation, provided the soil was not acid and was supplied with the necessary nutrients for the functioning of the azofiers. The azofiers are more resistant to these salts than are the ammonifiers, nitrifiers or most higher plants.

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